IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In the application of: Snow et al.
Serial No.: 09/544,344
Filed: 04/06/2000
For: MATERIALS, METHOD AND APPARATUS FOR DETECTION AND MONITORING OF CHEMICAL SPECIES
Examiner: Soderquist, Arlen
Art Group Unit: 1743

Honorable Commissioner of Patents
PO Box 1450
Alexandria, VA 22313-1450

DECLARATION UNDER 37 C.F.R. § 1.131 OF ARTHUR W. SNOW

Sir:

I, Arthur W. Snow, hereby declare that:

1. I am a joint inventor of the invention claimed in the above-identified patent application ("application").

2. Attached is a copy of portions of my invention disclosure, which formed the basis of the application.

3. The page titled "Patent Disclosure" bears a disclosure date of 05/15/1997. The contents of the disclosure were complete as of that date.

4. Attached are copies of pages from my laboratory notebooks dated 01/08/1997 and from 05/14/1997 to 06/20/1997. To the best of my recollection, all my research performed in the course of my full-time employment from 05/14/1997 to 06/20/1997 is documented in these pages.

5. Conception of the use of a coupling agent is documented on the notebook page dated 01/08/1997.

6. During the period of from 05/14/1997 to 06/20/1997, all of my research was concerned with encapsulated clusters, either as claimed in the application or directly or indirectly related to the claimed subject matter.

7. The entries of 06/20/1997 document the actual reduction to practice of the use of a coupling agent.

8. All work described in the disclosure and the notebook pages was performed in NAFTA or WTO member countries.

9. I further declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true, and further that these statements are made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

31 May 2007

Date

Arthur W. Snow

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

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PO Box 1450
Alexandria, VA 22313-1450

DECLARATION UNDER 37 C.F.R. § 1.131 OF HENRY WOHLTJEN

Sir:

I, Henry Wohltjen, hereby declare that:

1. I am a joint inventor of the invention claimed in the above-identified patent application ("application").

2. Attached is a copy of portions of my invention disclosure, which formed the basis of the application.

3. The page titled "Patent Disclosure" bears a disclosure date of 05/15/1997. The contents of the disclosure were complete as of that date.

4. Attached are copies of pages from the laboratory notebooks of co-inventor Arthur W. Snow dated 01/08/1997 and from 05/14/1997 to 06/20/1997.

5. Conception of the use of a coupling agent is documented on the notebook page dated 01/08/1997.

6. The entries of 06/20/1997 document the actual reduction to practice of the use of a coupling agent.

7. All work described in the disclosure and the notebook pages was performed in NAFTA or WTO member countries.

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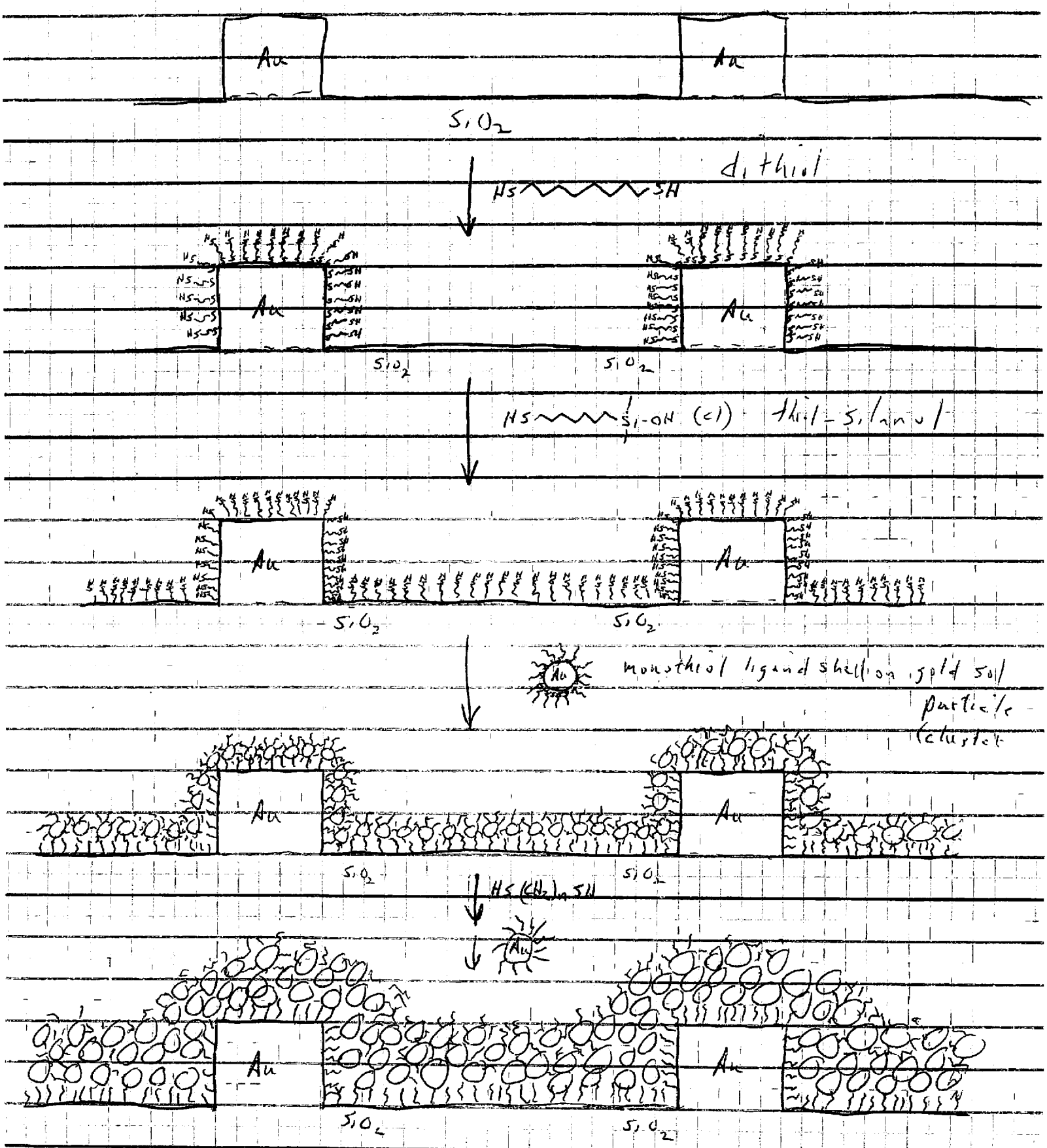
Code, and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

30 May 2007

Date

Henry Wohlgen

Approach for Thiol-gold sol Self Assembly on Gold/Quartz IDE Transdu



d and understood (obtain two signatures):

ness Date Signature Date 1-8-07

ness Date

NAVAL RESEARCH LABORATORY

LABORATORY RECORD

BOOK No. N-7950

Assigned to Arthur W Snow

Dates 3-12-97 to 5-20-97

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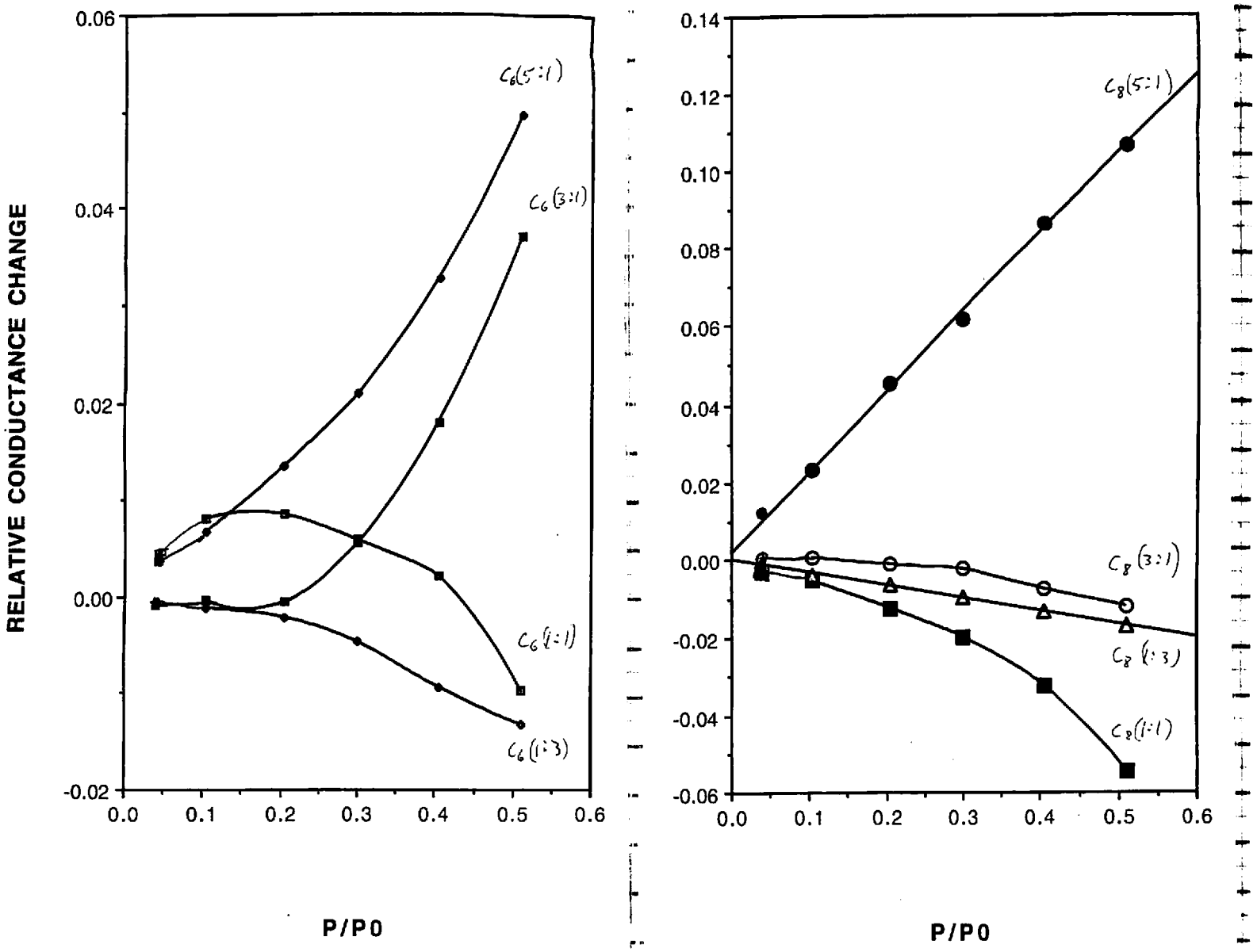


Trends appear to be as follows:

(1) Increasing chain length of ligand shell results in a decreasing and more negative response. The C_6 behavior is somewhat anomalous

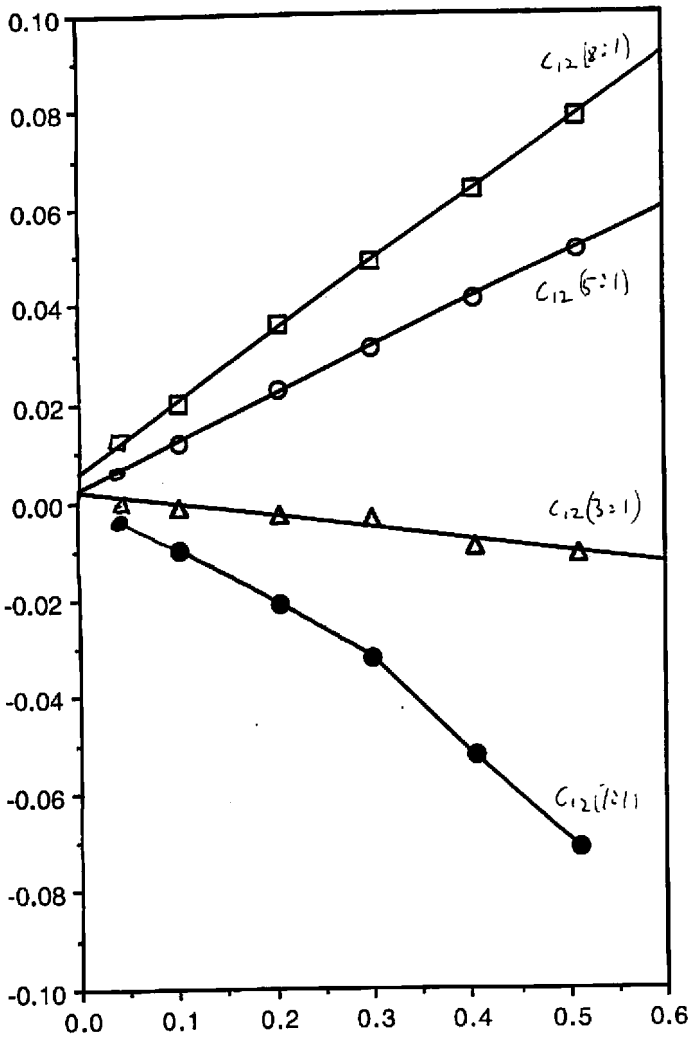
(2) The C_{16}, C_{12} and C_8 chain length ligand shells displayed reasonably good linearity in their isotherms, while the C_4 and C_6 were particularly non linear

(3) Large cluster cores promote positive sensor responses and small cores

Read and understood (obtain two signatures):

Witness _____ Date _____ Signature Arthur Shu Date 5-15-97

Witness _____ Date _____



promoted negative response (5 & 1-3 is an exception).

(4) 1:1 displays crossover behavior (negative → positive response with decreasing vapor concentration).

Read and understood (obtain two signatures):

Witness Date Signature Arthur Snow Date 5-15-93

Witness Date

Tetrachloroethylene Isotherm

Objective: Vapor Response mapping of $Au C_n(X:Y)$ to $CCl_2=CCl_2$

5V/100 KΩ Series	P/P°	Dilution Factor	Baseline	Signal	Signal/Baseline	Slope
						~~2.03 3.104~~ 2.6
Au C_8 (3:1)	.512	$(88)^3$	171952	69816	.5940	1.16
	.405	$(74)^3$	175332	93254	.4681	1.16
	.301	$(67)^3$	175298	109216	.3770	1.25
	.205	$(59)^3$	176668	130178	.2631	1.28
	.104	$(47)^3$	176814	150680	.1478	1.42
	.051	$(37)^3$	177522	164724	.0721	1.42
	.00:.125	$(05)^3$	177672	Δ=55	.00031	2.48
Au C_8 (1:1)	.512	$(80)^3$	21394	8419	.6065	1.18
	.405	$(73)^3$	21702	11192	.4843	1.20
	.301	$(67)^3$	21520	13224	.3855	1.28
	.205	$(59)^3$	21702	15790	.2724	1.33
	.104	$(47)^3$	21476	18246	.1504	1.45
	.051	$(37)^3$	21704	20080	.0748	1.48
	.00:125	$(05)^3$	21506	Δ=6	.00028	~~3.24~~
Au C_6 (1:1)	.512	$(80)^3$	126970	51852	.5916	1.16
	.405	$(74)^3$	129878	67292	.4819	1.19
	.301	$(67)^3$	129514	78852	.3912	1.30
	.205	$(59)^3$	130468	93416	.2840	1.39
	.104	$(47)^3$	130172	109244	.1608	1.55
	.051	$(37)^3$	130610	119808	.0827	1.63
	.00:125	$(05)^3$	129498	Δ=35	.00027	~~3.16~~
Au C_{12} (8:1)	.512	$(80)^3$	71694	34332	.5211	1.02
	.405	$(74)^3$	70830	41858	.4090	1.01
	.301	$(67)^3$	70840	48878	.3171	1.05
	.205	$(59)^3$	70754	54960	.2232	1.09
	.104	$(47)^3$	70720	62100	.1219	1.18
	.051	$(37)^3$	70816	66340	.0632	1.25
	.00:125	$(05)^3$	71860	Δ=12	.00017	~~1.35~~
Au C_{12} (5:1)	.512	$(80)^3$	30414	14784	.539	1.00
	.405	$(74)^3$	30146	17768	.4106	1.01
	.301	$(67)^3$	30208	20620	.3174	1.05
	.205	$(59)^3$	30128	23240	.2286	1.12
	.104	$(47)^3$	30178	26528	.1209	1.16
	.051	$(37)^3$	30152	28324	.0606	1.20

Read and understood (obtain two signatures):

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Witness _____ Date _____

0.5V/47 kΩ series

AuC_4 (1:1)	.512	$(80)^5$	180256	104194	.4220	.824
	.405	$(74)^3$	182514	122364	.3296	.814
	.301	$(67)^3$	183244	136202	.2567	.857
	.205	$(59)^3$	184416	151786	.1769	.863
	.104	$(47)^3$	185142	167148	.0972	.935
	.051	$(37)^3$	185482	175808	.0522	1.03
AuC_6 (5:1)	.512	$(80)^3$	176334	94686	.4630	.904
	.405	$(74)^3$	177036	113180	.3607	.891
	.301	$(67)^3$	177300	127760	.2794	.928
	.205	$(59)^3$	177346	142018	.1992	.972
	.104	$(47)^3$	177946	158712	.1081	1.04
	.051	$(37)^3$	179400	167222	.0574	1.13
AuC_6 (3:1)	.512	$(80)^3$	87934	39274	.5534	1.08
	.405	$(74)^3$	88710	48574	.4524	1.12
	.301	$(67)^3$	89108	56886	.3616	1.20
	.205	$(59)^3$	89386	65548	.2667	1.30
	.104	$(47)^3$	89862	76284	.1510	1.45
	.054	$(37)^3$	89898	82512	.0822	1.62
	.000125	$(05)^3$	89832	Δ=130	.00033	2.64
AuC_8 (5:1)	.512	$(80)^5$	56102	24580	.5619	1.10
	.405	$(74)^3$	55896	30342	.4572	1.13
	.301	$(67)^3$	55844	35702	.3607	1.20
	.205	$(59)^3$	56176	41370	.2636	1.27
	.104	$(47)^3$	56056	47900	.1455	1.40
	.051	$(37)^3$	56640	51742	.0767	1.51
	.000125	$(05)^3$	56768	Δ=16	.00028	2.24

5.0V/10 MΩ series

AuC_6 (1:3)	.512	$(80)^3$	203100	115090	.4333	.846
	.405	$(74)^3$	209954	135510	.3546	.876
	.301	$(67)^3$	212360	152768	.2806	.932
	.205	$(59)^3$	216044	171782	.2049	1.00
	.104	$(47)^3$	218466	194116	.1115	1.07
	.051	$(37)^3$	219352	206616	.0581	1.15
AuC_8 (1:3)	.512	$(86)^3$	35382	29858	.1561	.305
	.405	$(74)^3$	35370	31130	.1199	.296
	.301	$(67)^3$	35252	32162	.0877	.291
	.205	$(59)^3$	35352	32200	.0609	.297
	.104	$(47)^3$	35498	34394	.0311	.299
	.051	$(37)^3$	35544	34976	.0160	.316
AuC_{12} (1:1)	.512	$(80)^3$	45138	37050	.1792	.350
	.405	$(74)^3$	45386	38986	.1409	.348
	.301	$(67)^3$	45370	40658	.1039	.345
	.205	$(59)^3$	45394	42086	.0729	.356
	.104	$(47)^3$	45404	43692	.0377	.363
	.051	$(37)^3$	45344	44474	.0192	.379

Read and understood (obtain two signatures):

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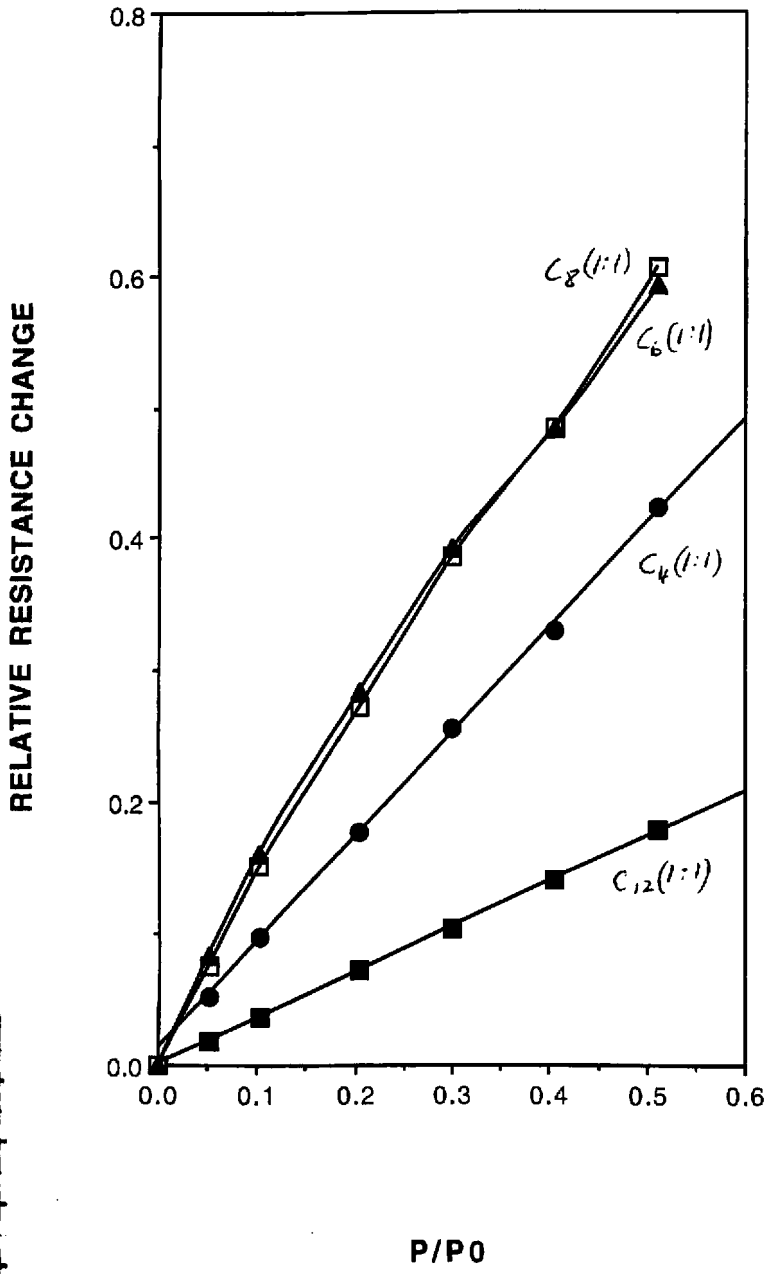
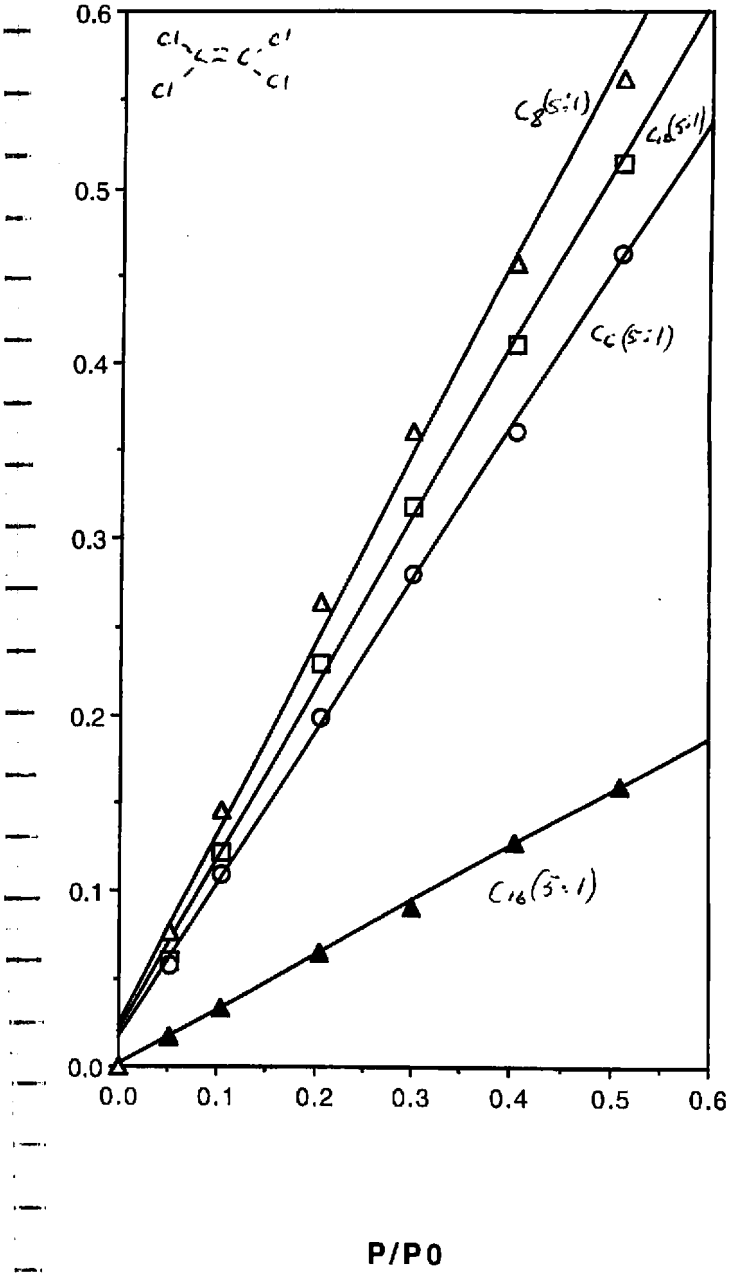
Witness _____ Date _____

Au C_{12} (3:1)	.512	$(80)^3$	133000	83766	.3702	.723
	.405	$(74)^3$	132836	92964	.3002	.741
	.301	$(67)^3$	133696	104124	.2212	.735
	.205	$(59)^3$	133358	112298	.1579	.770
	.104	$(47)^3$	134220	123324	.0808	.777
	.051	$(37)^3$	133744	128258	.0410	.809
Au C_{16} (5:1)	.512	$(80)^3$	52612	44190	.1601	.313
	.405	$(74)^3$	52702	45998	.1272	.314
	.301	$(67)^3$	52542	47816	.0899	.299
	.205	$(59)^3$	52652	49240	.0648	.316
	.104	$(47)^3$	52598	50846	.0333	.320
	.051	$(37)^3$	52748	51834	.0173	.342





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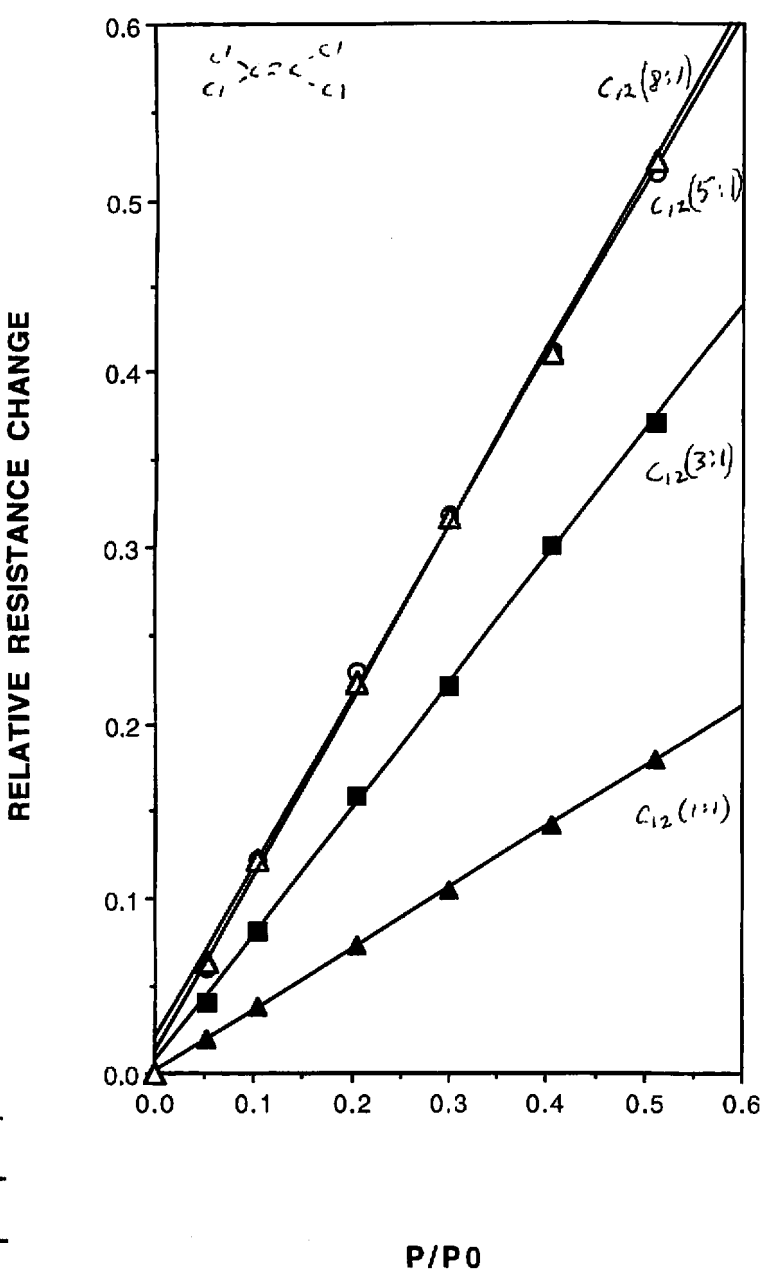
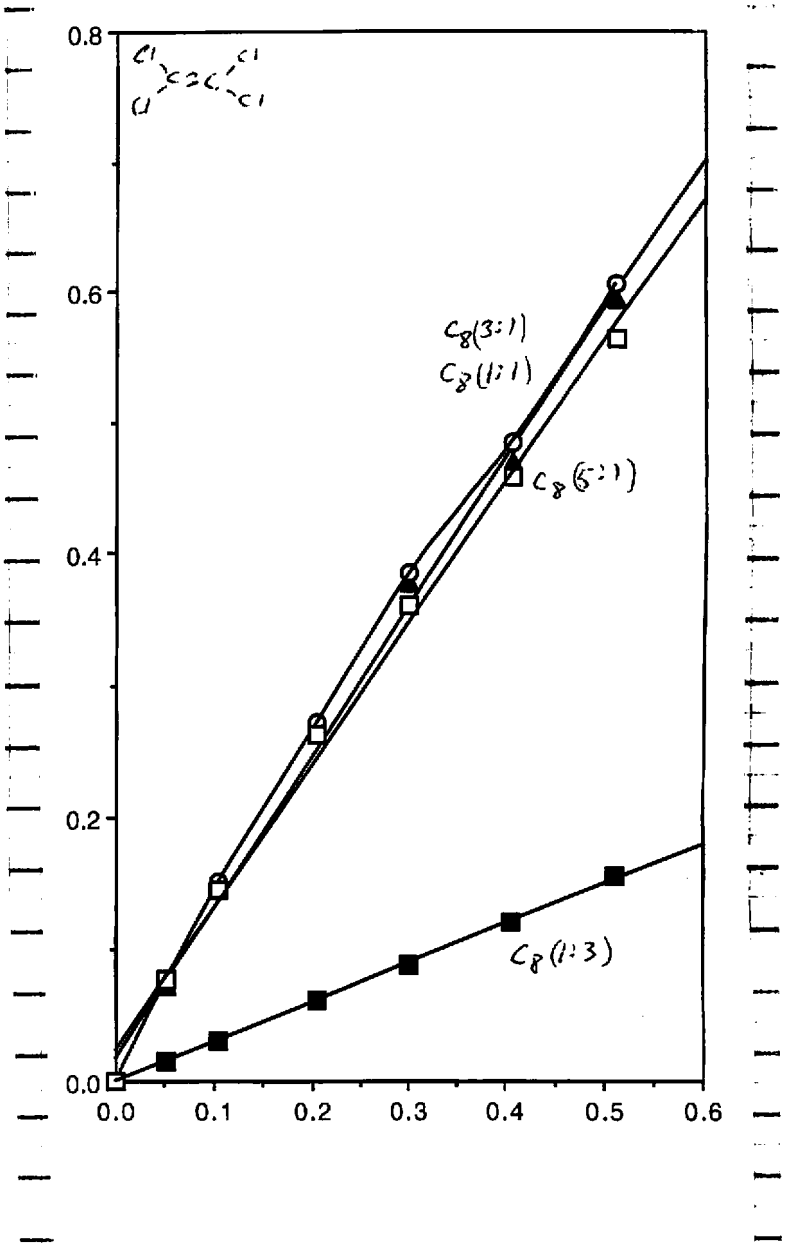
Witness _____ Date _____





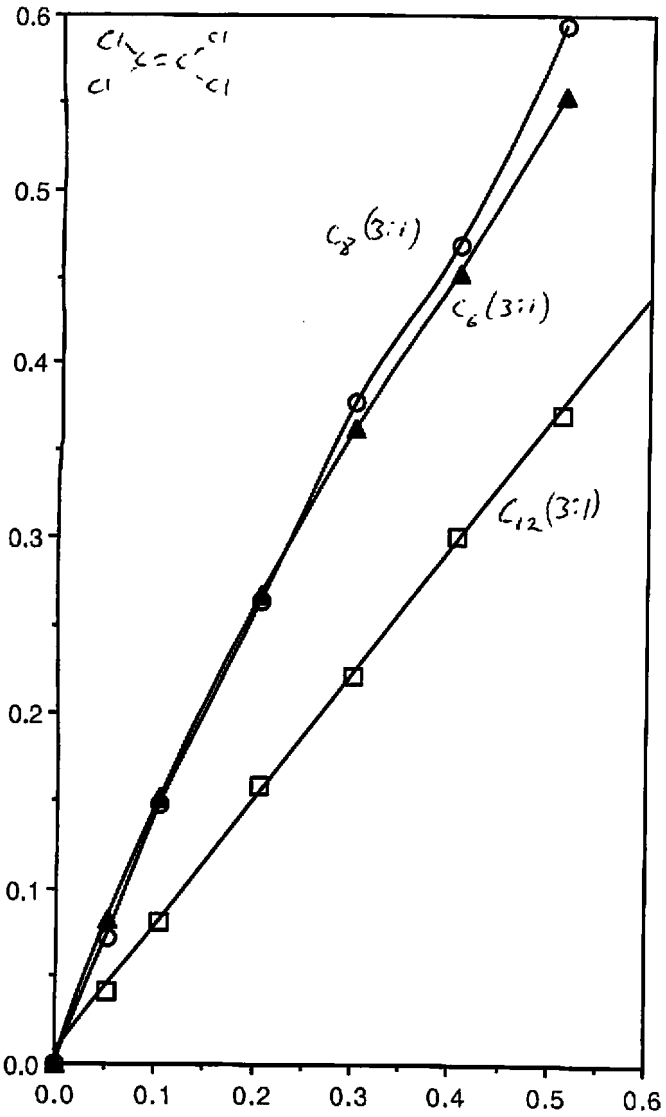
Response Table $\left(\frac{\Delta R/R}{(P/P_0)_{.10}}\right)$

C_n	1:3	1:1	3:1	5:1	8:1
C_{16}				.320	
C_{12}		.363	.777	1.16	1.18
C_8	.299	1.45	1.42	1.40	
C_6	1.07	1.55	1.45	1.04	
C_4		.935			

Read and understood (obtain two signatures):

Witness Date Signature Date 5-20-97

Witness Date



In slight contrast to toluene vapor response (N7950-73) the C_6 system is slightly more responsive to $ClCl_2=CCl_2$ than the C_8 system

Read and understood (obtain two signatures):

Witness Date Signature Arthur Snow Date 5-20-77

Witness Date

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BOOK No. N-7957

Assigned to Arthur Snow

Dates 5-16-97 to 7-19-97

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Au C_{12} (1:1) 20 → 120 → 20°C 5V DC Stability

Objective: Determination of effect of ~ 5.0 V bias on ~ 32 pass AuC_{12} (1:1) film conductivity through the 20 °C (1hr) → 120 °C (1hr) → 20 °C (1hr) cycle in comparison with the 0.05 V DC (N7942-53) and 5.0 volt AC (N7950-84) experiments.

An MSI 302 device was plasma cleaned and coated with a AuC_{12} 1:1 (10 mg/ml) via brushed deposition (32 passes) at 120°C and had an initial current of 0.36 nA (50 mV). The device was mounted on the substrate heater.

20 °C

time		I (nA)	time		I (nA)	time		I (nA)
18 45	0	37.30	19:46	61	161.83	20:46	121	182.5
18 46	1	35.67	19:47	62	168.00	20:47	122	140.02
18 47	2	35.26	19:48	63	169.88	20:48	123	114.62
18 48	3	35.06	19:49	64	171.98	20:49	124	99.34
1849	4	34.96	1950	65	173.47	20:50	125	89.58
1850	5	34.89	1951	66	175.26	20:51	126	82.88
1855	10	34.78	1952	67	177.11	20:52	127	78.51
1900	15	34.84	1953	68	178.94	20:53	128	75.56
1905	20	34.86	1954	69	180.89	20:54	129	73.34
1910	25	34.84	1955	70	182.61	20:55	130	71.83
1915	30	34.96	2000	75	192.12	21:00	135	68.18
1920	35	34.91	2005	80	200.16	21:05	140	67.00
1925	40	34.90	2010	85	209.4	21:10	145	66.31
1930	45	34.89	2015	90	218.1	21:15	150	66.08
1935	50	34.93	2020	95	226.4	21:20	155	65.79
1940	55	35.08	2025	100	235.2	21:25	160	65.57
1945	60	35.20	2030	105	242.7	21:30	165	65.35
20 → 120 °C			2035	110	250.7	21:35	170	65.12
			2040	115	258.0	21:40	175	64.88
			2045	120	264.8	21:45	180	64.70
			120 → 20 °C					

Read and understood (obtain two signatures):

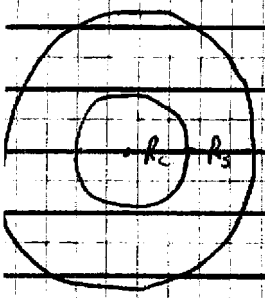
Witness _____ Date _____ Signature Catcher Shaw Date 5-16-97

Witness _____ Date _____

Calculations Related to Cluster Shell Volume and Thickness

Objective: Test relevancy of spherical model to Au C_n (X:Y) series.

Determine ligand shell thickness (R_s) from knowledge of core radius (R_c) and densities (ρ_c and ρ_s) and mass fractions (X_c and X_s) of core and ligand



$$X_s = \frac{M_s}{M_s + M_c} \qquad X_c = \frac{M_c}{M_s + M_c} \Rightarrow M_s = \frac{X_s}{X_c} M_c$$

$$V_s = \frac{M_s}{\rho_s} \qquad V_c = \frac{M_c}{\rho_c}$$

$$V_c = \tfrac{4}{3}\pi R_c^3 = \frac{M_c}{\rho_c} \Rightarrow M_c = \tfrac{4}{3}\pi R_c^3 \rho_c$$

$$V_s = \tfrac{4}{3}\pi (R_c + R_s)^3 - \tfrac{4}{3}\pi R_c^3 = \frac{M_s}{\rho_s} = \frac{1}{\rho_s}\frac{X_s}{X_c} M_c$$

$$\tfrac{4}{3}\pi (R_c + R_s)^3 - \tfrac{4}{3}\pi R_c^3 = \tfrac{4}{3}\pi R_c^3 \frac{\rho_c}{\rho_s}\frac{X_s}{X_c}$$

$$(R_c + R_s)^3 = \left(\frac{\rho_c}{\rho_s}\frac{X_s}{X_c} + 1\right) R_c^3$$

$$\left(\frac{R_c + R_s}{R_c}\right)^3 = \left(\frac{\rho_c}{\rho_s}\frac{X_s}{X_c} + 1\right)$$

$$\boxed{R_s = \left[\left(\frac{\rho_c}{\rho_s}\frac{X_s}{X_c} + 1\right)^{\frac{1}{3}} - 1\right] R_c}$$

For the Au and Cn this is

C_4	$\rho_s = .842$	Au	$\rho_c = 19.3$
C_6	$\rho_s = .838$		
C_8	$\rho_s = .843$		
C_{12}	$\rho_s = .845$		
C_{16}	$\rho_s = .848$		

} liquid density Fisher Thiols

ad and understood (obtain two signatures):

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Cn	1:3	1:1	3:1	(4:1)	5:1	8:1
C_{16}		.6588			.8346	
C_{12}	.7185	.7549	.7957	(.8427)	.8709	.8947
C_8	.7507	.8065	.8411		.9041	
C_6	.7922	.8241	.8835		.9192	
C_4		.8787				

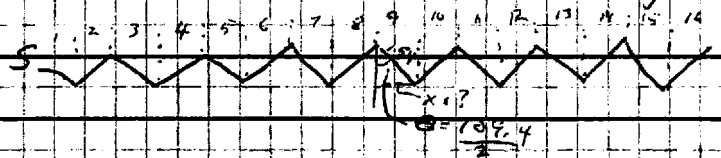
C_{16}		.81			2.83	
C_{12}	.86	1.14	1.56	(2.29)	2.97	3.61
C_8	.63	1.11	1.53		3.01	
C_6	.66	.96	1.61		2.92	
C_4		1.24				

C_{16}		1.09			2.18	
C_{12}	.99	1.18	1.40	(1.69)	1.89	1.97
C_8	.66	0.95			1.53	
C_6	.60	0.78			1.30	
C_4		0.75				

2.02
1.51
1.08
0.76
0.50

this extended chain length

Calculation of thiol extended chain length



$X = 1.54 \text{ Å} \sin \frac{109.4}{2} = 1.26 \text{ Å}$

$C_{16} = 16 \times 1.26 = 2.02$ nm
$C_{12} = 12 \times 1.26 = 1.51$ nm
$C_8 = 8 \times 1.26 = 1.08$ nm
$C_6 = 6 \times 1.26 = 0.76$ nm
$C_4 = 4 \times 1.26 = 0.50$ nm

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Witness _____ Date _____

③ Bondi Volume Equivalents Calculation V_B

Tables 14.12 14.1 14.1

$-S-(CH_2)_n-CH_3$

10.8 (10.23)$_n$ 13.67 $cm^3/mole \times \left(\frac{10^7 nm}{cm}\right)^3 \left(\frac{mole}{6.02\times10^{23}}\right)$ ↘

.0179 (.0170)$_n$ .0227 .0227 $nm^3/molecule$

C_n	16	12	8	6	4
V_B $nm^3/molecule$	.3126	.2446	.1766	.1426	.1086

④ Number of thiol ligands bonded to surface of Cluster N_S

$$N_S = 4\pi R_c^2 \rho_{HCP} \gamma$$

$\rho_{HCP} = 13.89$ atoms/nm^2

$\gamma = 0.66$ thiol bound/surface gold atom

example C_8 1:1

$$N_S = 4\pi (1.11\,nm)^2 \; 13.89 \frac{atoms}{nm^2} \times \frac{.568\ RSH}{Au\ atom} = 139 \text{ molecules RSA}$$

⑤ Van der Waals Volume V_{VDW} Calculation

$$V_{VDW} = N_S V_B = 139 \times .1766\ nm^3/molecule = 24.6\ nm^3$$

⑥ liquid density molecular volume of free thiols V_ρ

$$V_\rho = \frac{N_S}{\rho_{mol}} = \frac{139}{0.843\ g/cm^3} \left(\frac{cm}{10^7 nm}\right)^3 \times \frac{mole}{196.3\ g} \times \frac{6.02\times10^{23}\ molec}{mole} = \frac{139\ molec}{3.47\ molec/nm^3}$$

$= 40.1\ nm^3$

⑦ Free volume fraction f

$$f = 1 - \frac{V_{VDW}}{V_\rho} = 1 - \frac{24.6}{40.1} = .387$$

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Witness _____ Date _____

(3) Van Der Waal density of C_n thiols ρ_B

$$\rho_B = \frac{MW}{V_R}\Big/_{\rho_B} = \frac{14k.3\ g/mole}{1766\ nm^3/molecule \times \frac{6.02\times10^{23}\ molec}{mole} \times \left(\frac{cm}{10^7\ nm}\right)^3}$$

	C_{16}	C_{12}	C_8	C_6	C_4
MW	258.5	202.4	146.3	118.24	90.19
ρ_B	1.37	1.37	1.38	1.38	1.38

(4) Recalculation of R_{shell} using $\rho_s = 1.38$

$$R_s = \left[\left(\left(\frac{\rho_c}{\rho_s}\right)\left(\frac{x_c}{x_c}\right)+1\right)^{1/3}-1\right]R_c$$

	1:3	1:1	3:1	(4:1)	5:1	8:1	extended chain
C_{16}		.83			1.58		2.02
C_{12}	.74	.88	1.03	(1.22)	1.35	1.38	1.51
C_8	.49	.70	.82		1.07		1.08
C_6	.44	.56	.67		.89		.76
C_4		.53					.50

$\rho_s = 1.38$

Read and understood (obtain two signatures):

Witness _____ Date _____ Signature Graham Date 5-20-97

Witness _____ Date _____

Au S $C_2\phi$ (1:1)

$HAuCl_4$ +  $\xrightarrow[NaBH_4]{(C_8H_{17})_4NBr}$ $Au:C_2\phi$ (1:1)

Reagents

$(C_8H_{17})_4NBr$	3.42 g	(FW: 547)	6.25 mmol	Aldrich used as rec
Toluene	125 ml			Aldrich used as rec
$HAuCl_4 \cdot 3H_2O$	.5623 g	(FW = 394)	1.43 mmol	Aldrich used as rec
H_2O	47 ml			3x distilled
$C_6H_5CH_2CH_2SH$	.1982 g	(FW = 138.32)	1.43 mmol	Aldrich used as rec
Toluene	~0.5 ml			Aldrich used as rec
$NaBH_4$	.5912 g	(FW = 37.8)	15.6 mmol	Aldrich used as rec
H_2O	35.9 ml			3x distilled

Objective: Preparation aromatic alkyl thiol stabilized gold cluster to determine if aromatic functionality alters vapor response characteristics in microsensor study.

The solutions were prepared as indicated above. The $HAuCl_4/H_2O$ was prepared and handled in acid washed glassware.

To the $(C_8H_{17})_4NBr$/Toluene solution in a 500 ml Erlynmeyer was added the $HAuCl_4/H_2O$ solution with rapid stirring. After 1 min color disappearance from aqueous phase indicated transfer of the $HAuCl_4$. The ϕC_2SH was added with stirring - no significant color change occurred. With rapid stirring the $NaBH_4/H_2O$ was added (~15 sec) the mixture turned purple-black with gas effervescence. Rapid stirring was continued for (9:45 → 12:45) 3 hr.

The reaction was worked up by transfer to a 500 ml sep funnel and separation of the toluene phase in a 250 ml round bottom. This was concentrated (55°C/60 mm) to a 5-10 ml volume and ppt

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into 600 ml rapidly stirred MeOH. After settling for 1 hr, a clean separation occurred. The supernate was decanted and crude product collected by centrifugation. After drying at 30°C the product was redissolved in 5 ml toluene and dropwise into 200 ml rapidly stirred MeOH

After standing overnight at 10°C, the supernate was quite dark but centrifuging rendered a nearly colorless supernate. This is one of the cleanest separations on the 2nd gen to date. The product was collected by centrifugation, dried at 30°C and vacuum dried to yield 0.3146 g

Read and understood (obtain two signatures):

Witness Date Signature Arthur Chan Date 5-22-97

Witness Date

$Au C_2\phi$ 1:1 Toluene Isotherm

Objective: Obtain Toluene Vapor isotherm for comparison with Aliphatic $Au C_n$ (1:1) series

A 10 mg/ml stock solution (CHCl3) was prepared and air brushed onto a freshly plasma cleaned MSI 302 device (16 passes). The 50 mV current was 1.6 μA. Inspection with the optical microscope showed good coverage but a slightly more coarse texture

Initial Toluene vapor exposures at P/P0 .512 $(.80)^3$ for $Au C_2\phi$ (1:1) and $Au C_8$ (1:1) indicated the $Au C_2\phi$ had a slower response and 30, 60 and 120 exposure time cycles were run

exposure time	P/P0	dilution factor	Baseline	signal	Signal/baseline	$\frac{\Delta R/R}{P/P_0}$
$Au C_8$ (1:1)	5V/100 KΩ					
30 sec	.512	80 80 80	20954	7330	.6502	
60 sec	.512	80 80 80	20884	7380	.6468	
120 sec	.512	80 80 80	20784	7380	.6449	
120 sec	.405	74 74 74	20688	9106	.5598	
$Au C_2\phi$ (1:1)	0-5V 100 KΩ					
30 sec	.512	80 80 80	42452	24952	.41212	
60 sec	.512	80 80 80	41744	22480	.4615	
120 sec	.512	80 80 80	42064	21542	.48779	.953
120 sec	.405	74 74 74	42164	24288	.4240	1.047
120 sec	.301	67 67 67	41796	26844	.3577	1.188
120 sec	.205	59 59 59	41740	29940	.2827	1.379
120 sec	.104	47 47 47	41904	33862	.1919	1.845
120 sec	.0507	37 37 37	42058	36806	.1249	2.463
120 sec	.0244	29 29 29	42112	38852	.07741	3.173
120 sec	.0138	24 24 24	42170	39938	.05293	3.835
120 sec	.00805	20 20 20	42262	40704	.03687	4.608
120 sec	.00416	16 16 16	42314	41332	.02321	5.660

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Witness _____ Date _____ Signature Arthur Chu Date 5-23-97

Witness _____ Date _____

120 Sec	.00173	12 12 12	42352	41830	.01233	7.124	
120 Sec	.000512	8 8 8	42360	42172	.004438	8.668	} repeat
120 Sec	.000125	5 5 5	42366	42312	.001275	10.20	

$CCl_2=CCl_2$ Isotherm

Au $C_2\phi$ (1:1) 0.5 V/100 KΩ

120 Sec	.512	80 80 80	41.438	21860	.4725	.923
120 Sec	.405	74 74 74	41438	24486	.4091	1.010
120 Sec	.301	67 67 67	41572	27686	.3340	1.110
120 Sec	.205	55 55 55	41856	30.594	.2691	1.313
120 Sec	.104	47 47 47	41.958	35.044	.1648	1.584
120 Sec	.0507	37 37 37	42208	37754	.1055	2.081
120 Sec	.0244	29 29 29	42406	39662	.06471	2.652
120 Sec	.0138	24 24 24	42528	40722	.04267	3.077
120 Sec	.000800	20 20 20	42644	41438	.02828	3.535
120 Sec	.000416	16 16 16	42592	41876	.01681	4.100
120 Sec	.00173	12 12 12	42606	42264	.008027	4.640
120 Sec	.000512	8 8 8	42620	42548	.002628	5.133
120 Sec	.000125	5 5 5	42628	42580	.000891	7.13

$CH_3CH_2CH_2OH$ Isotherm (Au: $C_2\phi$ (1:1))

720 Sec	.512	80 80 80	43082	41576	.03496	.06827
120 Sec	.405	74 74 74	43052	42002	.02439	.06022
120 Sec	.301	67 67 67	42968	42274	.01615	.05366
120 Sec	.205	55 55 55	42820	42498	.009832	.04796
120 Sec	.104	47 47 47	42836	42634	.004716	.04534
120 Sec	.0507	37 37 37	42774	42660	.002665	.05257
120 Sec	.0244	29 29 29	42720	42650	.001639	.06715
120 Sec	.0138	24 24 24	42668	42624	.001031	.07473

H_2O Isotherm (Au $C_2\phi$ (1:1))

120 Sec	.804	93 93 93	42478	-4.5x25	-.00265	
120 Sec	.614	85 85 85	42578	~~-4.0x25~~ -3.1x25	~~-.00225~~ -.00146	
120 Sec	.405	74 74 74	42430	-1.9x25	-.000790	
120 Sec	.205	59 59 59	42388	-1.0x25	-.000447	
120 Sec	.104	47 47 47	42318	0	0	

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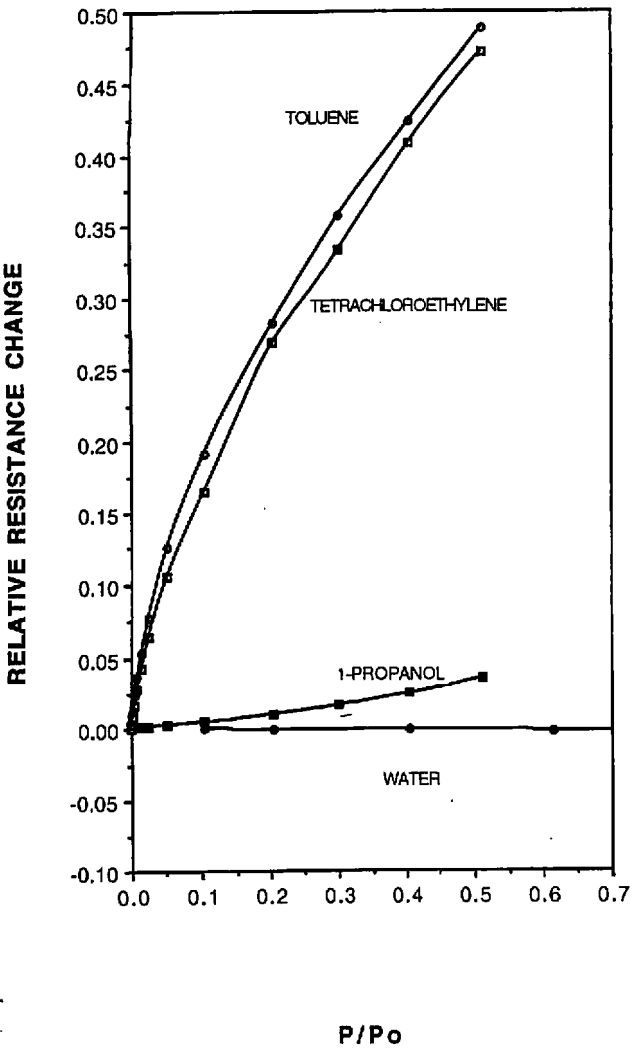
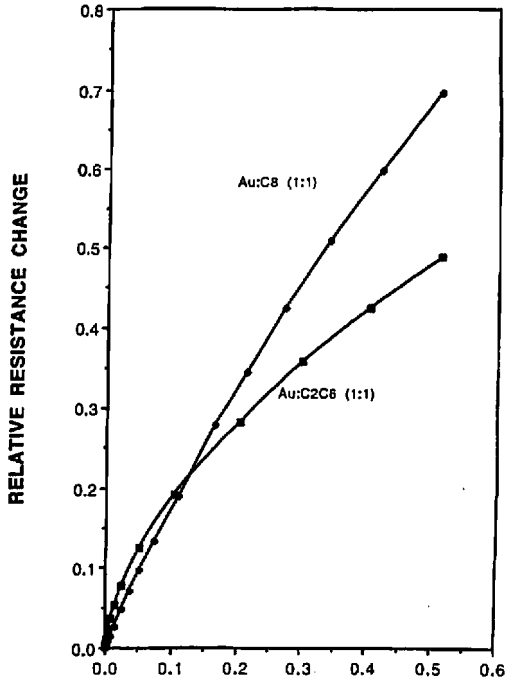
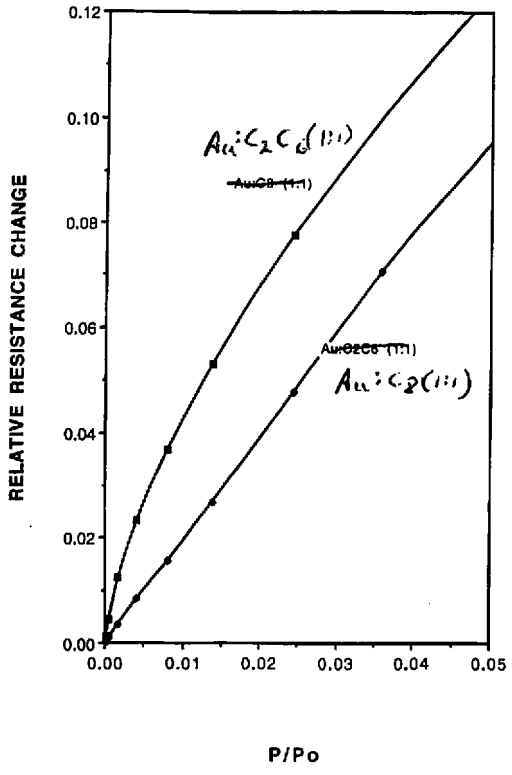
Witness _____ Date _____

Au:C2C6(1:1) ISOTHERM DATA



COMPARISON OF AU:C2C6(1:1) VS AU:C8(1:1) RESPONSES TO TOLUENE VAPOR





ad and understood (obtain two signatures):

itness _____ Date _____ Signature _____ Date 6-15-97

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Au 5 C, ϕ (1:1)

$HAuCl_4$ + ⬡CH_2SH $\xrightarrow[NaBH_4]{(C_8H_{17})_4NBr}$ Au : C, ϕ (1:1)

Reagents

$(C_8H_{17})_4NBr$	3.42 g	(FW = 547 g/mol)	6.25 mmol	Aldrich (used as rec)
Toluene	125 ml			Aldrich (used as rec)
$HAuCl_4 \cdot 3H_2O$	0.5632 g	(FW = 354 g/mol)	1.43 mmol	Aldrich (used as rec)
Water	47 ml			3x distilled
$C_6H_5CH_2SH$	0.1772	(FW = 124.21 g/mol)	1.43 mmol	Aldrich used as rec
Toluene	~0.5 ml			Aldrich used as rec
$NaBH_4$	0.5906	(FW = 37.8 g/mol)	15.6 mmol	Aldrich used as rec
H_2O	39.5 ml			3x distilled

Objective: Preparation of benzyl thiol stabilized gold cluster for comparative vapor response measurement with the Au:$C_2\phi$ and Au:C_8 (1:1) systems in microsensor study

Solutions were prepared as indicated above. The $HAuCl_4/H_2O$ soln was prepared and handled in acid washed glassware.

To the $(C_8H_{17})_4NBr$/Tol soln in a 500 ml Erlynmeyer was added the $HAuCl_4/H_2O$ with rapid stirring. After 2 min when color of toluene and H_2O phases indicated phase transfer had occurred the ϕCH_2SH/toluene was added (no significant color change observed). With very rapid stirring the $NaBH_4/H_2O$ was added (ice cold) with observation of purple color formation and effervescence. Rapid stirring was continued for (13:20 → 16:20) 3 hr.

The reaction was worked up by transferring to a 500 ml sep funnel, and separating the toluene phase into a 250 ml round bottom

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Witness Date

flask. This was concentrated to a ~10-12 ml volume and ppt by dropwise addition into 600 ml rapidly stirred MeOH. After 3hr stand at rm temp a good settling occurred. The supernate was decanted and crude product collected by centrifugation. This product was dissolved in ~4 ml (not quite soluble in 3 ml) and ppt into 200 ml rapidly stirred MeOH. Rapid settling did not occur in this and suspension was allowed to stand at 10°C overnight.

Supernate remained highly colored. Centrifugation at 6000 rpm/2min was attempted - supernate remained very dark At 6000 rpm/10 min produced a better result with a transparent but dark supernate. The product was collected by 6000 rpm/10 min centrifugation. The product was dried at 30°C the vacuum dried for 2 hr yield 0.269 g

ead and understood (obtain two signatures):

itness _____ Date _____ Signature Arthur Shaw Date 5-27-97

itness _____ Date _____

Au:C_{12} (4:1) 3rd Reppt Purification and Temperature-Conductivity Measurements

Objective: Obtain better Temp-Conductivity data on Au C_{12}(4:1) - The instability of the measurements (N7250-75 & N7250-42) appeared to indicate that the sample (N7250-40) may lack sufficient purity - possibly some $(C_8H_{17})_4NBr$ contamination and a third reprecipitation into MeOH might improve stability of these measurements. The entire product (N7250-40) was dissolved in ~3 ml toluene and ppt dropwise into 200 ml rapidly stirred (freshly opened MeOH. After standing overnight at 10°C, the supernate remained highly colored. Centrifuging for 15 min/6000 rpm produced a low quality separation with the product poorly packed at the bottom of the tube and a strongly colored but transparent supernate. It was decided to attempt product collection with these conditions. During the last centrifuge spin the tube failed but product could be recovered. This was transferred to the original vial and vacuum dried.

A sample was prepared for -76 → 40°C conductivity measurements. A 10.0 mg/ml Au:C_8(4:1)/$CHCl_3$ solution was prepared and air brushed ~~16 passes~~ onto a 120°C MSI 302 (plasma cleaned) device.

~~Probe~~ Initial current 50 mV = 17 nA.

I(nA)	T(°C)	I(nA)	T(°C)	I(nA)	T(°C)	I(nA)	T(°C)	I(nA)	T(°C)	
4.775	-76.2	7.490	-57.9	10.819	-38.0	15.052	-10.1	16.809	14.8	
5.030	-74.2	7.710	-56.5	11.199	-35.9	15.135	-9.1	17.030	17.4	
5.281	-72.6	7.892	-55.3	11.375	-35.0	15.228	-8.1	17.381	22.3	slow drift
5.522	-71.0	8.143	-53.8	11.552	-34.0	15.413	-5.8	17.67	27.4	
5.643	-70.2	8.387	-52.2	11.735	-33.0	15.472	-5.0	17.93	29.3	
5.783	-69.0	8.610	-50.8	11.919	-32.0	15.724	-3.0	18.64	34.7	
6.101	-67.0	8.894	-49.0	12.175	-30.6	15.928	-0.1	19.24	38.1	
6.261	-66.0	9.135	-47.5	12.984	-25.7	16.910	2.6	19.45	44.1	
6.406	-65.0	9.433	-45.9	13.264	-23.9	16.151	5.1			
6.636	-63.5	9.657	-44.5	13.476	-22.6	16.231	7.2			
6.869	-62.0	9.859	-43.3	13.733	-20.9	16.367	9.0			
7.095	-60.5	10.148	-41.6	14.045	-18.6	16.505	11.2			
7.321	-59.0	10.654	-39.0	14.944	-11.2	16.655	13.1	slow resistance drift		

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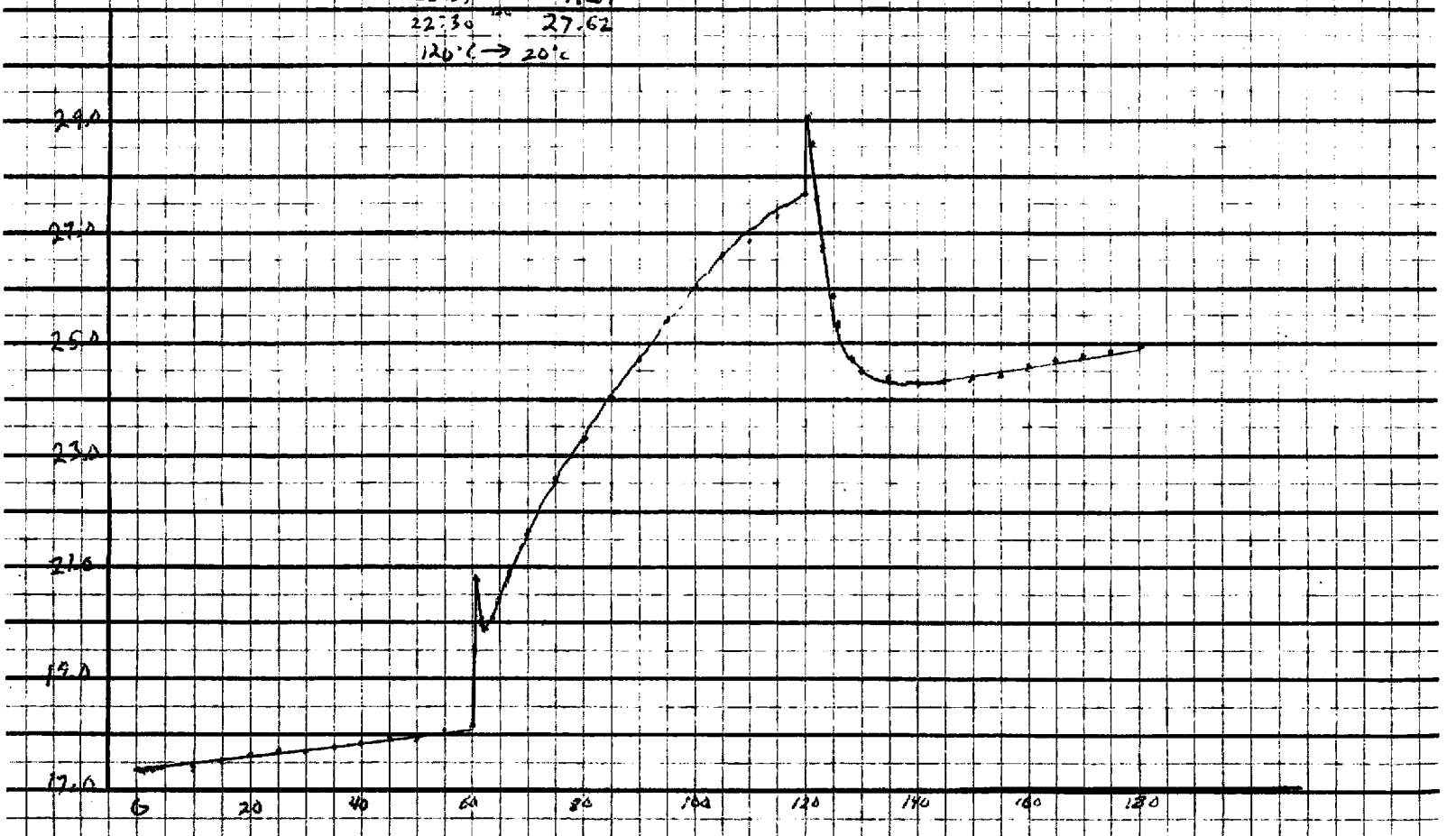
Witness _____ Date _____ Signature Arthur Snow Date 5-25-57

Witness _____ Date _____

20° → 120 → 20°C Thermal Cycle Stability expt

Same sample as Variable temperature expt (Preceding Page)

time	I (nA)	time	I (nA)	time	I (nA)
20:30	17.40	21:31	20.83	2231	29.03
20:31	17.39	21:32	20.06	22:32	28.57
20 32	17.38	21:33	19.95	22:33	27.60
20 33	17.41	21:34	20.12	22:34	26.66
20 34	17.42	21:35	20.46	22:35	25.91
2035	17:43	21:36	20.70	22:36	25.35
2040	17.44	21:37	20.93	22:38	24.75
2045	17.50	21:38	21.18	22:40	24.48
2050	17.60	21:39	21.41	22:45	24.31
2055	17.70	21:40	21.62	22:50	24.26
2100	17.68	21:45	22.54	22:55	24.32
2105	17.74	21:50	23.24	23:00	24.39
2110	17.85	21:55	24.01	23:05	24.47
2115	17.95	22:00	24.73	23:10	24.58
2120	17.97	23:05	25.43	23:15	24.69
2125	18.03	22:10	26.01	23:20	24.80
2130	18.12	22:15	26.52	23:25	24.89
20°C → 120°C		22:20	26.88	23:30	25.00
		22:25	27.29		
		22:30	27.62		
		120°C → 20°C			



Read and understood (obtain two signatures):

Witness _____ Date _____ Signature Arthur Snow Date 5-28-97

Witness _____ Date _____

$Au_5 C_1 \phi OCH_3$ (1:1)

$$HAuCl_4 + CH_3O\text{-}\phi\text{-}CH_2SH \xrightarrow[NaBH_4]{(C_8H_{17})_4NBr} Au:C_1\phi OCH_3$$

Reagents:

$(C_8H_{17})_4NBr$	3.42 g	(FW = 547 g/mol) 6.25 mmol	Aldrich used as rec'd
Toluene	125 ml		Aldrich used as rec'd
$HAuCl_4 \cdot 3H_2O$	.5591	(FW = 394 g/mol) 1.42 mmol	Aldrich used as rec'd
Water	47 ml		3 × distilled
$pCH_3O\,C_6H_4CH_2SH$	.2189	(FW = 154.23 g/mol) 1.42 mmol	Aldrich used as rec'd
Toluene	~1 ml		Aldrich used as rec'd
$NaBH_4$	.5863	(FW = 37.8 g/mol)	Aldrich used as rec'd
Water	39 ml		3× distilled

Objective: Preparation of the methoxy functionalized benzyl thiol gold cluster for comparative vapor response measurement with the more hydrophobic cluster system.

Solutions were prepared as indicated above. The $HAuCl_4/H_2O$ solution was prepared and handled in acid washed glassware.

To the $(C_8H_{17})_4NBr$/Toluene solution in a 500 ml Erlenmeyer was added the $HAuCl_4/H_2O$ solution with rapid stirring. After ~2 min when color of aqueous (clear) and toluene (dark brown) phases indicated $AuCl_4^-$ transfer had occurred. The $CH_3O\phi CH_2SH$ was added - no observable color change observed. With very rapid stirring the $NaBH_4/H_2O$ solution was added over a 15 sec interval - Rapid purple-black coloration developed and mild effervescence of hydrogen. Rapid stirring was continued for (13:10 → 16:10) 3 hr.

The reaction was worked up by transferring to a 500 ml

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Witness _____ Date _____

Sep Funnel and separating the toluene phase into a 250 ml round bottom flask. This was concentrated to a ~10 ml volume (55°C/60 Torr) and ppt by dropwise addition into 600 ml MeOH.

After 4hr standing a good settling had occurred and a relatively clear supernate was decanted and the crude product collected by centrifugation and dried at 30°C. This crude product was redissolved in 3-5 ml toluene and reppt by dropwise addition to 200 ml rapidly stirred MeOH. A clouded suspension formed and was placed in a refrigerator overnight (10°C)

After standing 10 hr at 10°C the supernate remained highly colored. Centrifugation of the supernate (6000 rpm/25min) separated much of the solid leaving a brown but transparent supernate. The purified product was isolated by centrifuging the 200 ml, and finally washed with 15 ml MeOH, centrifuged, dried at 35-40°C transferred to a vial and vacuum dried overnight yield 0.2830 g

It was observed during cleanup that this cluster complex is significantly soluble in acetone.

ad and understood (obtain two signatures):

tness _____ Date _____ Signature Cynthia Jones Date 6-2-97

tness _____ Date _____

Detection of Trace Organic in Aqueous Condensed Phase with Au:C$_8$ 1:1 Chemiresistor

Objective: Demonstration that this alkanethiol stabilized gold cluster chemiresistor will respond to trace organic dissolved in water. The alkanethiol stabilized gold clusters are very hydrophobic, and hypothesis is that there will be a strong chemical potential for a dissolved trace organic such as toluene to partition into the cluster deposition which should respond in similar manner as to toluene vapor. The following experiment is designed to demonstrate the phenomena and possibly the sensitivity.

The Au:C$_8$(1:1) cluster was selected as a very toluene sensitive candidate with strong hydrophobicity.

Au C$_8$ 1:1 / MS1302 devices were prepared as follows. The (4) MS1302 devices were inspected (50X), checked for shorts and plasma cleaned.

A 10 mg/ml stock solution of Au C$_8$(1:1) N7542-41 was prepared. Two of the devices were mounted on a resistive heater, heated to 120°C and sprayed with an airbrush (finest nozzle setting) with 16 1-sec passes. The second pair of devices was done in likewise fashion. Current measurements (50mV) were made in each device and are designated as follows:

Au C$_8$ 1:1 #1	Au C$_8$ 1:1 #2	Au C$_8$ 1:1 #3	Au C$_8$ 1:1 #4
33.7 nA	28.1 nA	24.6 nA	33.7 nA

Read and understood (obtain two signatures):

Witness Date Signature Arthur Snow Date 6-2-97

Witness Date

A saturated solution of toluene in water was prepared by placing ~1.5 ml water (3x distilled) in a 2.5 ml vial and adding ~4 drops Toluene (99.9+% Aldrich) and stirring gently for ≥3 hr. The solubility of toluene in water is 0.0515 %W (Riddick & Bunger) A series of dilutions from this saturated solution were made as follows

T_0	Saturated	0.0515
T_1	$\frac{.2078 g T_0 (.0515)}{.2078 g + 1.8076} =$	0.00531
T_2	$\frac{.2219 g T_1 (.00531)}{.2219 g + 1.8727} =$	0.000563
T_3	$\frac{.2160 g T_2 (.000563)}{.2160 g + 1.9682} =$	0.0000530

The experimental test was conducted by placing a quantity of water or the Tol/H_2O solutions in a 10x75 mm tube up to a level to just immerse the electrode area

Au C_8/// #4 37.1 33.14 nA in AIR @ 50mV DC

H_2O immersion 51.5 nA in Dist. H_2O

35.42 ~~34.81~~ nA in AIR

T_3 ~ 45 nA ±3 in .0000530% Toluene

(120 nA - 140 nA) in Dist. H_2O (drifting down)

~ 32 nA in AIR

T_2 137 nA ± in T2 .000563 %

28.7 nA in AIR

133 ± 2 nA in H_2O

28.7 nA in AIR

T_1 110 nA in T1 .00538 % (drifting down)

30.2 nA in AIR

125 nA in Dist. H_2O

26 nA in AIR

T_0 48 nA in T0 0.0515 %

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Witness Date Signature Date 6-2-77

Witness Date

DIST H_2O – 149 nA

TØ – 53 nA

DIST. H_2O – 185 nA

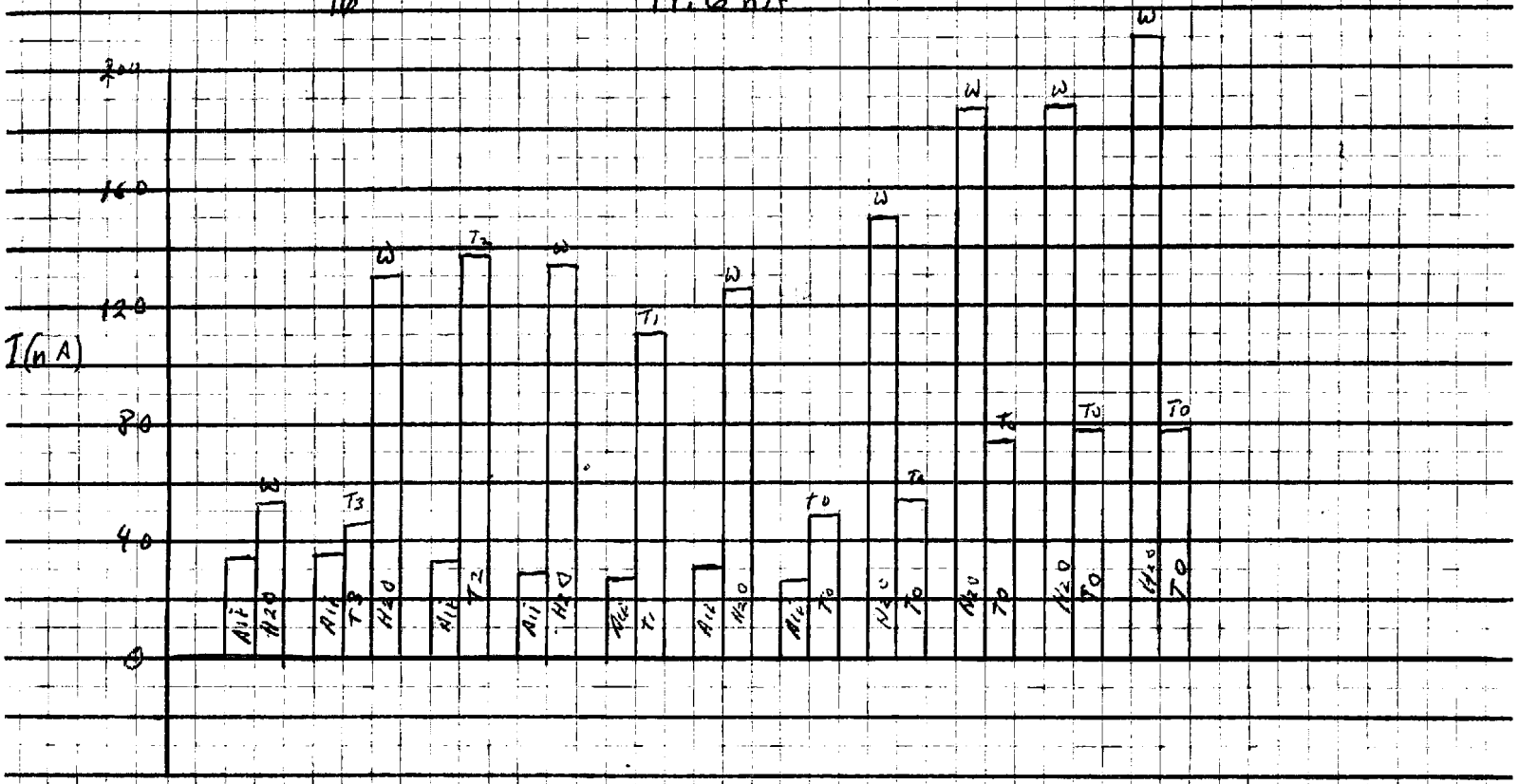
TØ – 73.6 nA

DIST H_2O – 186 nA

TØ – 78.4 nA

DIST. H_2O – 210 nA

TØ – 77.6 nA



It appears that water ~~exposure~~ immersion after a moderate conditioning time results in an increase in conductivity of almost one of magnitude (ie 30 nA → 200 nA). Removal from the water and a min or two to dry reverts the conductivity to the 25-30 nA range. Immersion in a toluene saturated water solution (0.051% w/w) causes the conductivity to decrease to the 70-80 nA level on at least 3 to four repetitions. Clearly the toluene causes a strong decrease in conductivity. This cycling causes some deterioration of the film. Optical microscope observation shows a lot of microcracking in addition to lift of several portions of the film. Treatment of the film with a dithiol (eg $HS(CH_2)_6SH$) might solve this problem.

Read and understood (obtain two signatures):

Witness Date Signature Arthur Chen Date 6-3-97

Witness Date

I-V Curve Data on $Au C_n(X:Y)$

Objective: Collective summary of ±2 V I-V Ohms law demonstration for devices prepared for utilization in Vapor response study

ie N7550-38 etc

V(volts)	C_{12}(1:3)	C_{12}(1:1)	C_{12}(3:1)	C_{12}(4:1)	C_{12}(5:1)	C_{12}(8:1)	C_{16}(5:1)	C_8(1:3)	C_8(1:1)
			nA	nA	nA	nA	nA	nA	nA
0	-25 pA	-10 pA	.163	.589	3.55	9.48	.041	.014	3.98
.05	74 pA	.136 nA	1.48	5.33	31.59	83.92	.41	.160	35.2
.10	165 pA	.275	3.01	10.82	64.28	170.9	.83	.327	71.5
.20	.322 nA	1.35	6.06	21.95	129.76	343.7	1.67	.662	144.1
.30	.461 nA	2.17	9.22	34.40	198.25	526.2	2.55	1.007	218.7
.40	.601 nA	2.54	12.31	49.28	262.5	700.7	3.39	1.335	291.1
.50	.728 nA	3.65	15.38	54.95	327.2	873.5	4.18	1.656	362.8
.60	.852 nA	4.30	18.43	65.6	392.7	10.48	5.01	1.980	435.2
.70	1.001 nA	4.98	21.68	77.2	461.4	1231	5.90	2.321	511.1
.80	1.15 nA	5.60	24.81	88.9	527.0	1406	6.73	2.645	583.7
.90	1.28 nA	6.24	27.85	100.3	592.0	1579	7.54	2.967	655.2
1.00	1.40 nA	6.98	31.01	112.8	657.6	1754	8.36	3.300	727.4
1.2	1.78 nA	8.32	37.90	140.0	792.1	2114	10.11	4.001	875.1
1.4	2.11 nA	9.59	44.15	166.4	923.0	2462	11.82	4.707	1018
1.6	2.51 nA	11.07	50.89	194.0	1058	2871	13.61	5.459	1165
1.8	2.91 nA	12.54	57.35	222.0	1192	3176	15.42	6.227	1309
2.0	3.22 nA	13.93	63.97	249.4	1327	3535	17.27	7.003	1454
0	-28 pA	-8 pA	.148	.51		9.48	.037	.010	3.88
-.05	-103 pA	-.46	-1.40	-5.52	3.52	-78.06	-.40	-.151	-31.8
-.10	-176 pA	-.78	-2.92	-11.35	-219.28	-165.5	-.82	-.307	-67.4
-.20	-.335 nA	-1.57	-6.12	-23.20	-62.06	-350.3	-1.70	-.634	-142.0
-.30	-.472 nA	-2.26	-9.17	-34.25	-130.7	-525.1	-2.52	-.943	-214.6
-.40	-.606 nA	-2.93	-12.19	-45.24	-196.2	-698.1	-3.35	-1.248	-285.1
-.50	-.733 nA	-3.62	-15.22	-56.41	-262.5	-873.0	-4.17	-1.556	-356.6
-.60	-.870 nA	-4.34	-18.45	-67.78	-328.0	-1056	-5.04	-1.882	-431.5
-.70	-.971 nA	-4.95	-21.50	-78.39	-396.6	-1231	-5.87	-2.196	-503.2
-.80	-1.07 nA	-5.60	-24.58	-89.35	-462.1	-1404	-6.69	-2.512	-574.3
-.90	-1.18 nA	-6.22	-27.67	-100.98	-526.9	-1580	-7.50	-2.835	-646.1
-1.0	-1.31 nA	-6.81	-30.99	-113.5	-592.5	-1763	-8.38	-3.178	-721.3
-1.2	-1.58 nA	-8.20	-37.48	-138.9	-661.4	-2112	-10.08	-3.839	-863.8
-1.4	-1.87 nA	-9.58	-44.08	-166.2	-792.0	-2471	-11.84	-4.538	-1010
-1.6	-2.18 nA	-10.90	-51.61	-193.6	-926.7	-2826	-13.60	-5.245	-1154
-1.8	-2.53 nA	-12.32	-57.26	-222.9	-1060	-3185	-15.40	-5.980	-1300
-2.0	-2.89 nA	-13.90	-63.54	-250.8	-1195	-3534	-17.22	-6.711	-1440
					-1327				
	m=1.46	m=6.92	m=31.6	m=120	m=661	m=1764	m=8.50	m=3.33	m=724
	b=.048	b=.010	b=.048	b=-.078	b=-.163	b=.554	b=.0088	b=.061	b=3.63
	V_0=-.033	V_0=-.0014	V_0=-.0015	V_0=+.00065	V_0=.00025	V_0=-.00031	V_0=.00010	V_0=.018	V_0=.0050
5m .4μ	1.2×10^{-9}	5.6×10^{-9}	3×10^{-8}	1×10^{-7}	5×10^{-7}	1×10^{-6}	7×10^{-9}	3×10^{-9}	6×10^{-7}
2μ	2.3×10^{-9}	1.1×10^{-8}	5.0×10^{-8}	1.9×10^{-7}	1.1×10^{-6}	2.8×10^{-6}	1.4×10^{-8}	5.3×10^{-9}	1.2×10^{-6}

Read and understood (obtain two signatures):

Witness _____ Date _____ Signature Tuthin Date 6-4-97

Witness _____ Date _____

Calculation of σ, Vapor response devices are 16 post settings $\pm\left(\frac{1}{2}\ 32\ \text{posts} \times .4\mu\right) \cdot 2\mu$

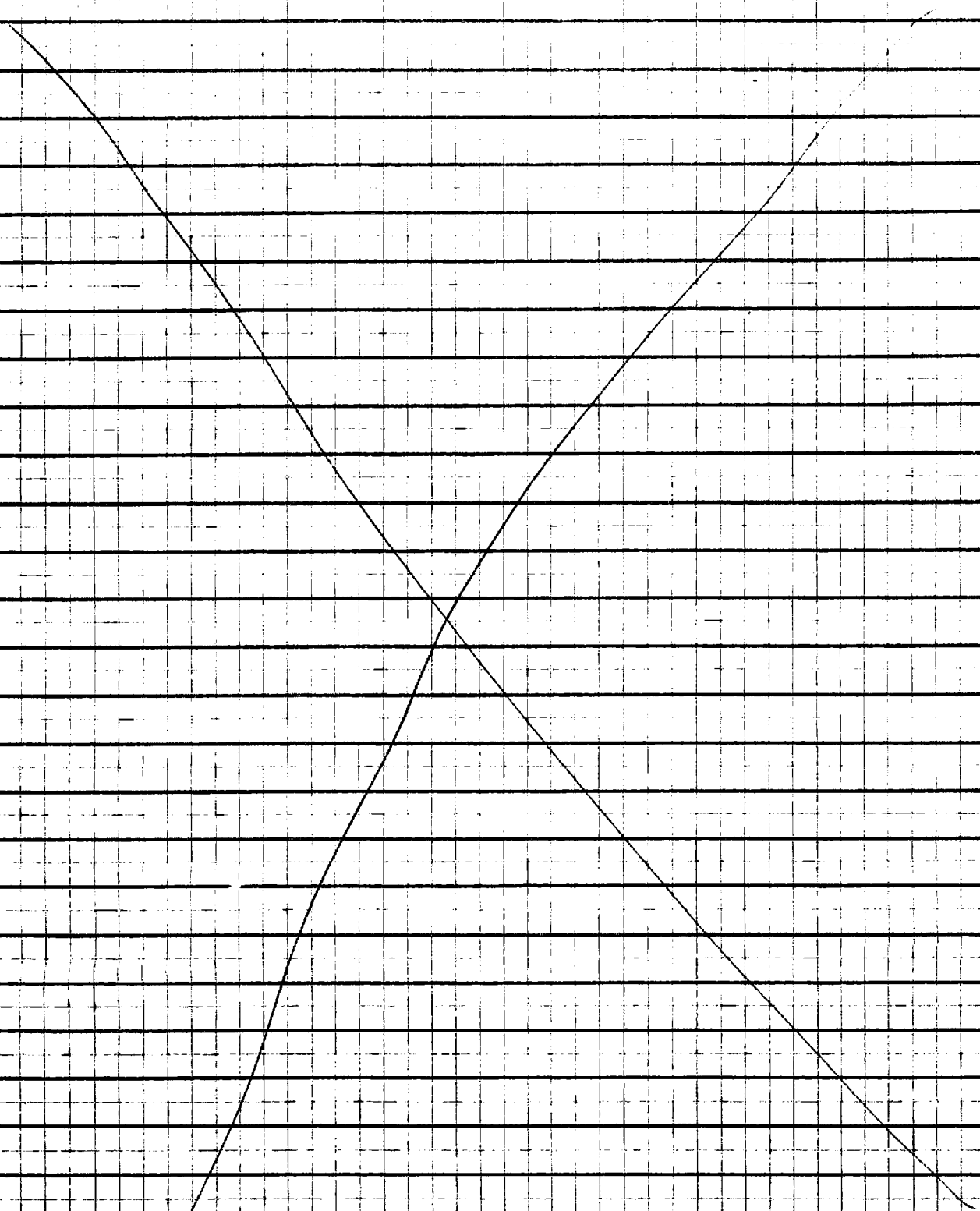
$$\sigma = \frac{d}{2(n-1)l}\frac{1}{n}\frac{I}{V} = \frac{15\mu}{2(50-1)\,4800\mu}\ .2\mu\ \frac{cm}{10^4\mu}\ \frac{I}{V} = 1.59\left(\frac{I}{V}\right)$$

(3:1)	C_8(5:1)	C_6 (1:3)	C_6(1:1)	C_6(3:1)	C_6 (5:1)	C_4 (1:1)	
nA	nA	nA	nA	nA	nA	nA 1188	
24.8	512	.274	18.73	782	2190	~~1680~~	
09.6	4530	2.44	166.0	6954	19446	10635	
27.3	9217	4.95	336.1	14137	39540	21650	
6 27	18593	9.96	677.2	28510	79740	43690	
318.6	28410	151.19	1034.5	43576	121830	66830	
7543	37790	20.15	1376.2	57940	161990	88980	
2187	47070	25.04	1715.7	72220	200600	110890	unstable
2623	56450	29.95	2060	86670	240700	133050	rapid increase
3083	66280	35.09	2423	101,880	282800	156360	measurement
3524	75680	40.00	2770	116450	322900	178700	taken after 15sec
3960	84970	44.80	3113	130700	362500	199800	
4403	94360	49.66	3462	144900	402600	223700	
5305	113600	59.65	4174	174990	484860	273100	
6185	132290	69.45	4869	263000	564800	323000	
7089	151580	79.52	5590	238300	647100	375500	
7979	170640	89.45	6308	272500	728400	428100	
8879	189940	99.50	7030	305900	810700	482200	
23.5	514	.255	18.02	817	2180	1282	
192.9	.4186	-2.13	-150.0	+6714	-17900	-10580	
109.6	-8886	-4.50	-319.5	-14219	-37930	-22420	
260.7	-18729	-9.47	-670.9	-29920	+79930	-47220	
291.2	-28110	-14.20	+1006.2	-44880	-119980	-77890	
717.5	-37400	-18.88	-1338.0	-59660	-159606	-94300	
1149	-46800	-23.60	-1675.8	-74580	-199686	-117940	
1602	-56640	+28.54	-2031	-90210	-243000	-142650	
2036	-66030	-33.25	-2373	-105100	-283000	-166280	
2467	-75330	+37.92	+2712	-119790	-322600	-189486	
2904	-84730	-42.62	-3059	-134770	-362700	-214660	
3365	-94580	-47.58	+3422	-150310	-404700	-240360	
3245	-113280	-57.02	+4106	-179800	-484506	-286700	
4143	-132550	-66.77	-4810	-211900	-566006	-334706	
5030	-151590	-76.43	-5515	-243806	-647900	-384600	
5928	-170890	-86.22	-6232	-276600	-730300	-437600	
6803	-189640	-95.76	-6926	-308900	-810200	-488800	
1400	m = 94700	m = 48.7	m = 3460	m = 150480	m = 404380	m = 237170	
2.04	b = 85.9	b = .855	b = 23.4	b = -1500	b = 144	b = -4071	
046	V_0 = .00095	V_0 = -.018	V_0 = +.0068	V_0 = +.010	V_0 = -.00036	V_0 = +.017	
10^{-6}	8×10^{-5}	4×10^{-8}	3×10^{-6}	1×10^{-4}	3×10^{-4}	2×10^{-4}	
10^{-6}	1.5×10^{-5}	7.8×10^{-8}	5.5×10^{-6}	2.4×10^{-4}	6.4×10^{-4}	3.8×10^{-4}	

Read and understood (obtain two signatures):

Witness _____ Date _____ Signature _____ Date 6-4-96

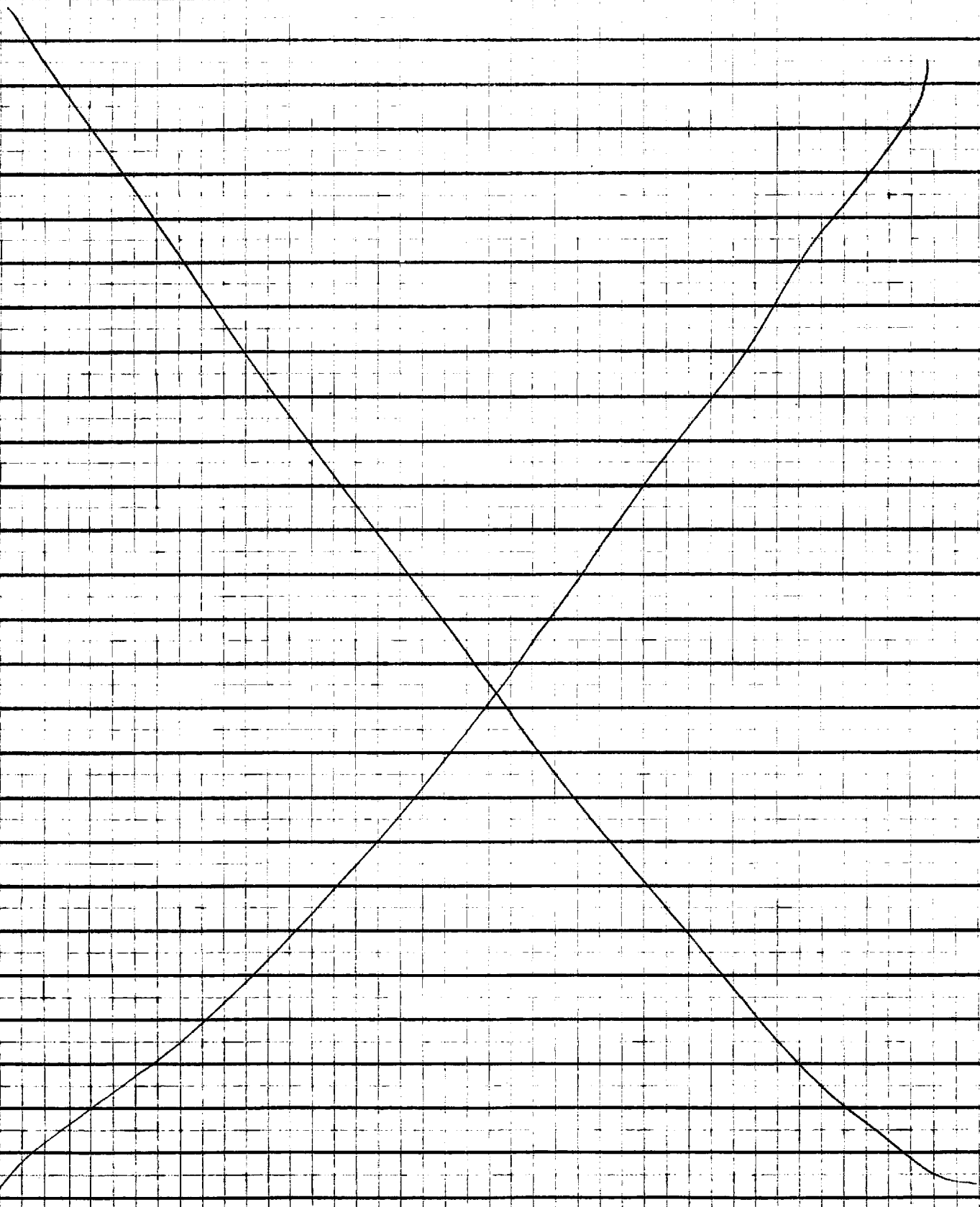
Witness _____ Date _____



Read and understood (obtain two signatures):

Witness _____ Date _____ Signature _____ Date _____

Witness _____ Date _____



Read and understood (obtain two signatures):

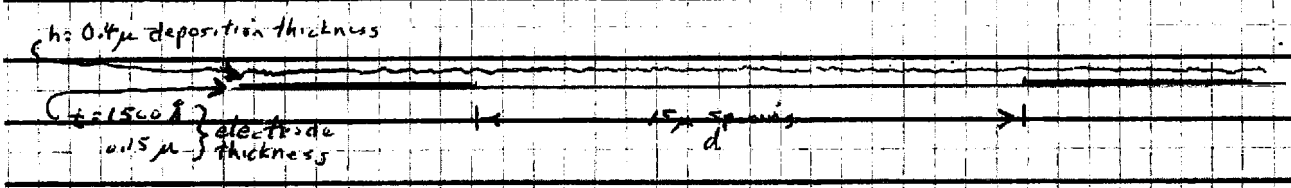
Witness Date Signature Date

Witness Date

Interdigital Electrode Analysis

Objective: Assessment of deposition thickness effect relative to electrode thickness and spacing.

Scale Perspective on MSI 302 device



Film thickness - 32 passes (1sec) with air brush using 10 mg/ml sol'n
- Weight increase on device is 0.0001 g
- device dimensions $12.5\text{ mm} \times 7.0\text{ mm} \times \left(\frac{\text{cm}}{10\text{ mm}}\right)^2 = 0.875\text{ cm}^2$

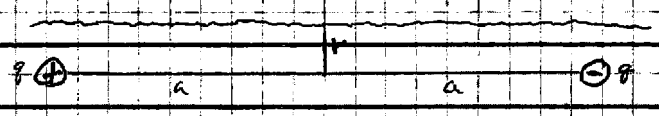
$$\text{Thickness} = \frac{0.0001\text{ g}}{0.875\text{ cm}^2} \times \frac{\text{cm}^3}{3.06\text{ g}} \times \frac{10^4\,\mu}{\text{cm}} = 0.4\,\mu$$

ρ: 3.06 JACS 117, 12537 (1995) $AuCl_2$ (1:1)

$$\sigma = \frac{d}{2(n-1)\ell} \frac{1}{h} \frac{1}{V} = \frac{15}{2(50-1)\,480} \frac{1}{.4\mu \times \frac{\text{cm}}{10^4\,\mu}} \times \frac{1}{.054} = 15.94\left(\frac{1}{\Omega\text{cm}}\right)$$

Consider edge of electrode a point charge separated by a 15μ spacing

Then use Halliday & Resnick (p. 762) solution for an electric field surrounding a dipole



$$E = \frac{1}{4\pi\epsilon_0} \frac{2aq}{(a^2+r^2)^{3/2}}$$

at $r=0$ (in plane of electrode)

$$E = E_0 = \frac{1}{4\pi\epsilon_0} \frac{2aq}{a^3}$$

Then the ratio of the field, E', at $r=h$ to the field E_0 at $r=0$ is

$$\frac{E'}{E_0} = \frac{\frac{1}{(a^2+h^2)^{3/2}}}{\frac{1}{a^3}} = \frac{a^3}{(a^2+h^2)^{3/2}} = \frac{1}{\left(\frac{a^2+h^2}{a^2}\right)^{3/2}} = \frac{1}{\left(1+\left(\frac{h}{a}\right)^2\right)^{3/2}}$$

in our model $a = \frac{d}{2}$

$$\frac{E'}{E^0} = \frac{1}{\left(1+\left(\frac{2h}{d}\right)^2\right)^{3/2}}$$

Calculation for $d = 15\mu$ and h varying from 0.4μ to 15μ

$h(\mu)$	0.4	1.0	2.5	5.0	7.5	10.0	15.0
E'/E_0	0.996	0.974	0.854	0.576	0.354	0.216	0.089
h/d	0.027	0.067	0.167	0.333	0.500	0.667	1.000

*Note as d becomes smaller, a thinner film is necessary to preserve the same level of accuracy e.g. $d = 5\mu$ $E'/E_0 = 0.963$ at $h = 0.4\mu$

Read and understood (obtain two signatures):

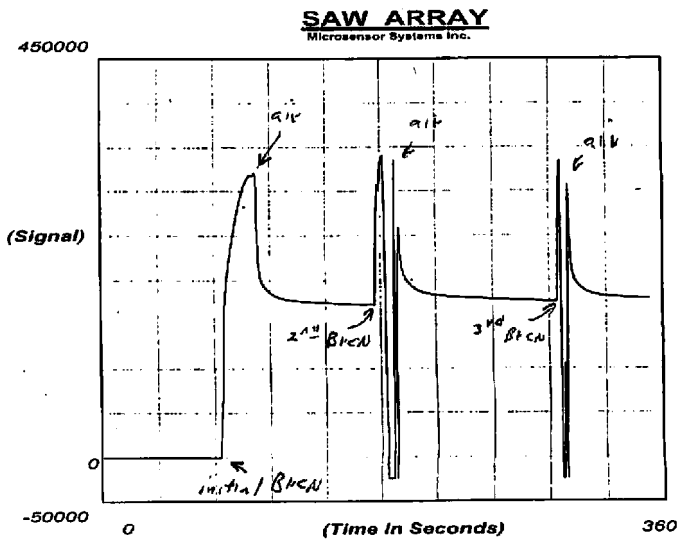
Witness _____ Date _____ Signature Arthur Snow Date 6-4-97

Witness _____ Date _____

Cyanogen Bromide Response of $Au C_8$ 1:1 Sensor

Objective: Determination if and to what degree the alkanethiol stabilized gold cluste chemiresistor sensor will respond to cyanogen bromide. The BrCN is a substitute for the chloride analog for which similar activity would be predicted. The long term objective is an effective sensor for cyanogen chloride

Cyanogen Bromide was procured from Aldrich. A few crystals were placed in a 25 ml erlynmeyer which was fitted with a two hole rubber stopper through which tubing would conduct compressed air in and BrCN vapor out and to the cell containing the $Au:C_8(1:1)/MS1302$ sensor. BrCN has a 20°C vapor pressure of 82.5 mm Hg and the $BrCN_{vapor}$ and compressed air purges were alternately passed through the cell at a flow rate of ~15 cm^3/min.



Initial exposure to the BrCN caused a large increase in the conductivity. It amounted to a 6.5x50,000 = 325,000 Hz signal increase (baseline was not recorded). The first purge 3.8x50,000 = 190,000. The second BrCN exposure increased the signal to an off-scale value but the second air purge returned the conductivity level to the baseline corresponding to that before the 2nd BrCN exposure. Likewise, a third BrCN exposure sent the conductivity level to a value off scale and purge returned it to its previous baseline.

The sensor used was that of $Au C_8(1:1)$ #2 N74501-38 which was previously characterized by an 50 mV current measurement. Another measurement was made at the new baseline. The conductivity change is as follows:

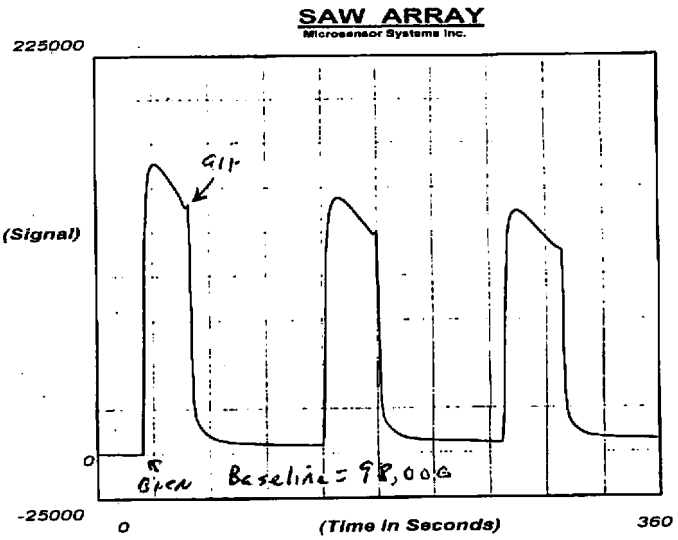
Read and understood (obtain two signatures):

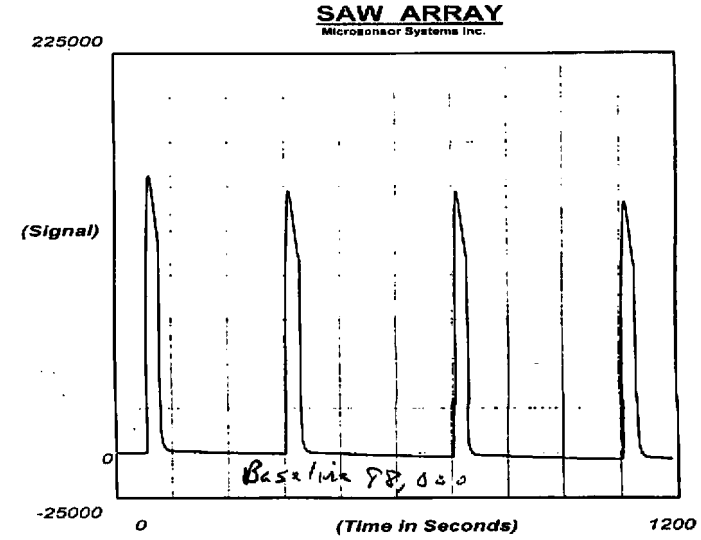
Witness _____ Date _____ Signature Arthur Snow Date 6-4-97

Witness _____ Date _____

33 nA (50 mV) before BrCN exposure → 250 nA (50 mV) after BrCN exposure

After adjustment of the voltage & resistance of the AC circuit the BrCN response was kept on scale and exposed response was measured for several cycles each time returning to the same baseline (98,000). The response is extremely fast and strong. Repeated exposures had an apparent decline in signal response intensity. This proved to be more a result of evaporation rate of the BrCN crystal being too slow for the flow rate through the flask. The sensor was allowed to set for 2 hr. Exposures were then timed for a 30 sec duration during which the signal follows the exponential dilution in the BrCN flask followed by a six minute purge - allowing greater time for BrCN recovery. The signal in this case did not diminish with repeated exposure.





Signal = 6 × 25000 = 150,000

Signal / baseline = 150,000 / 98,000 = 1.53

$n_{BrCN} / n_{air} = 82.5 / 760 = 0.109 = 1.09 \times 10^{5} / 10^{6} = 109{,}000$ ppm

assuming linearity 1.53 fract. change / 109,000 ppm = 0.00014 fract. change / ppm, i.e. 0.014% change / ppm

i.e. 100 ppm should produce a 1.4% conductivity change

Read and understood (obtain two signatures):

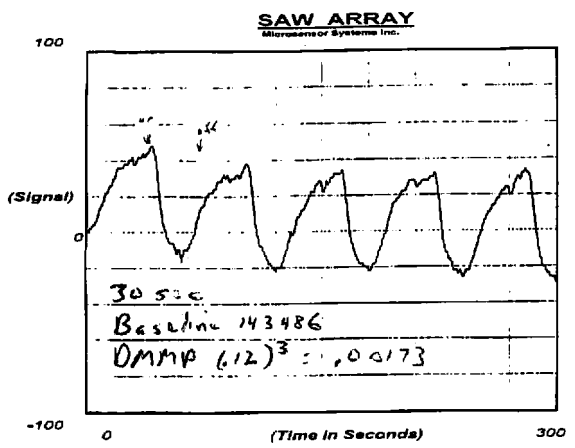
Witness _____ Date _____ Signature Arthur Snow Date 6-4-97

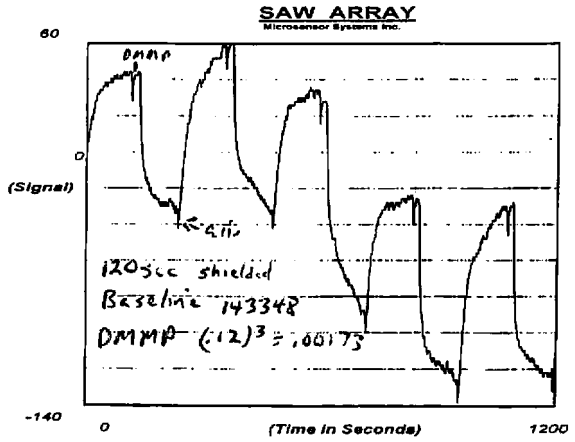
Witness _____ Date _____

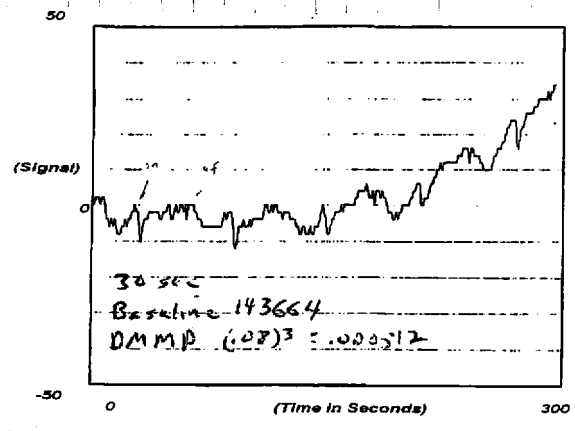
DMMP Response of Au:C_8 1:1

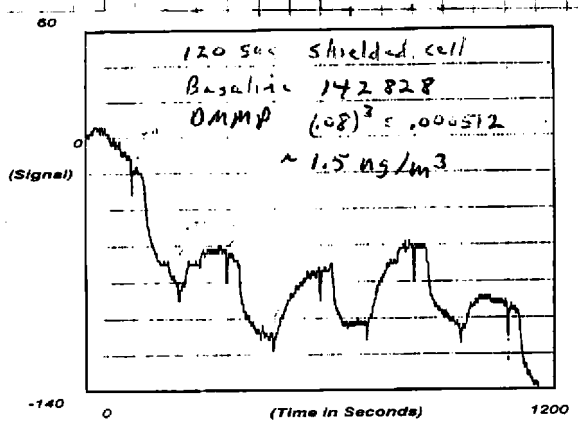
Objective: Determine sensitivity limit of generic alkanethiol stabilized gold cluster sensor to dimethylmethylphosphonate (DMMP).

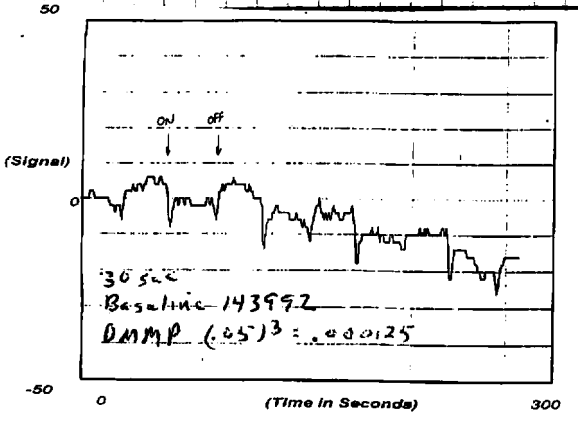
The AuC_8 (1:1) /MSI 302 device was mounted in the vapor exposure cell and connected to the vapor generator by a minimum tube length.

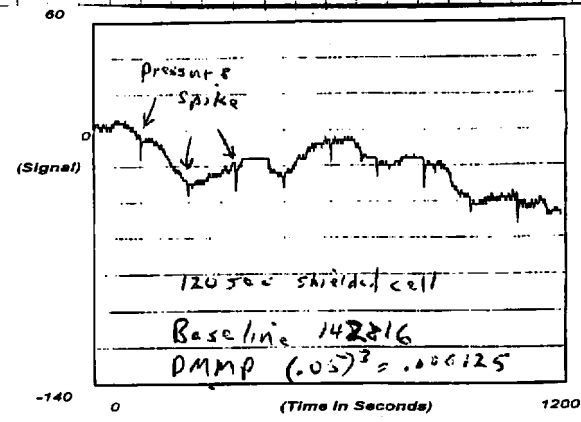












Read and understood (obtain two signatures):

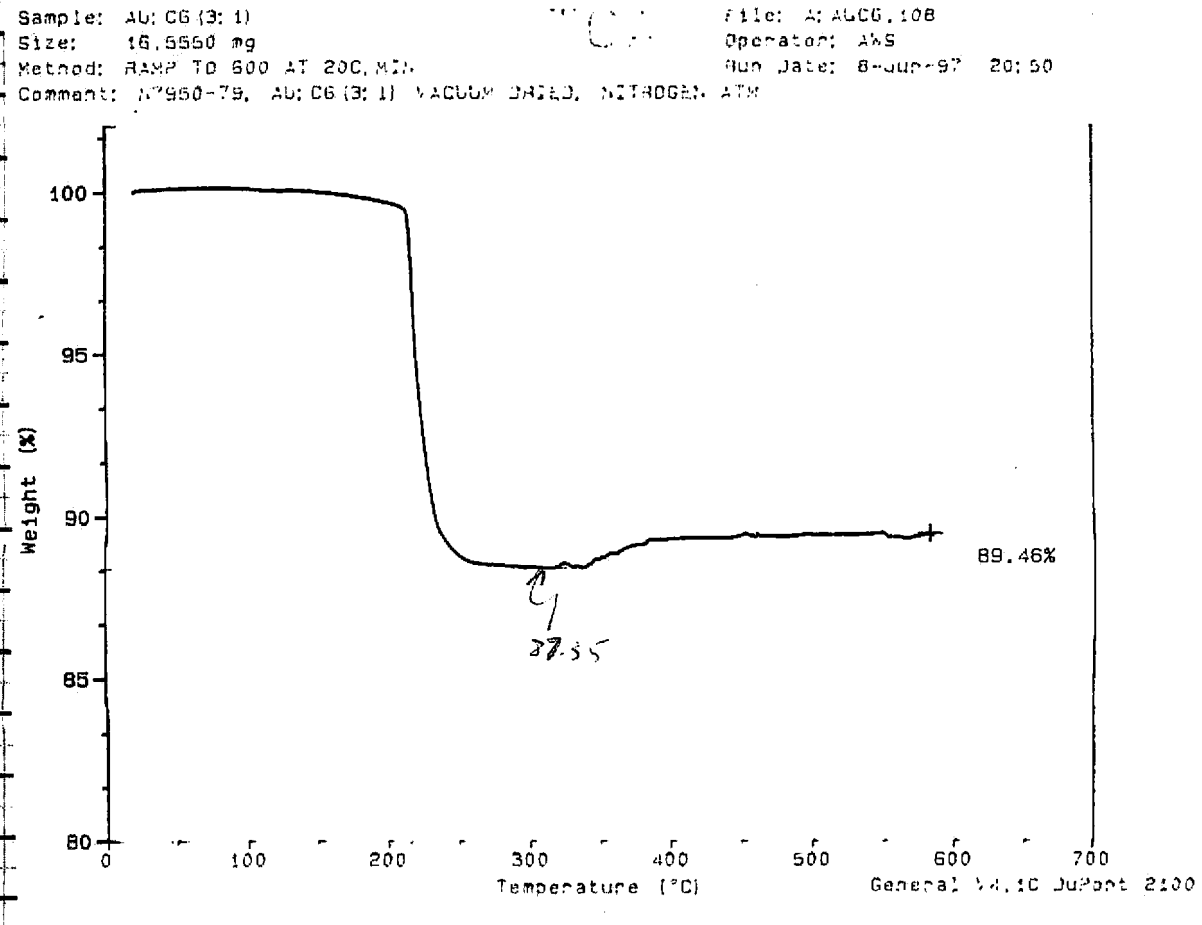
Witness Date Signature Date 6-4-15

Witness Date

TGA of $Au C_6$ (3:1), $Au C_8$ (3:1)
$Au C_2\phi$ (1:1), $Au C_1\phi$ (1:1) and $Au C_1\phi OMe$

TGA's were run at 20°C/min under N_2 on 15 - 20 mg samples

Sample	AuC_6 (3:1)	$Au C_8$ (3:1)	$Au C_2\phi$ (1:1)	$Au C_1\phi$ (1:1)	$Au C_1\phi OMe$
File name	AuC6.108	AuC8.105	$Au C_2C_6$.101	$Au C_1C_6$.101	AuC_1C_6OME.101
W_{Au}					

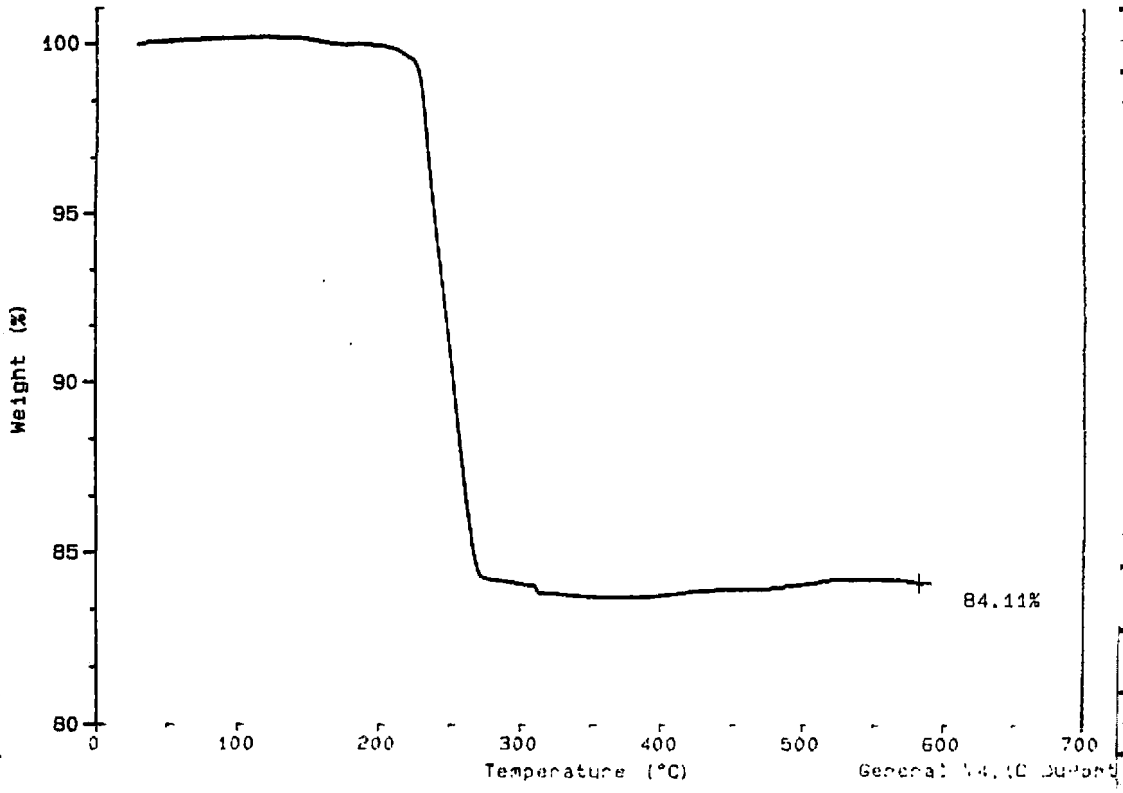


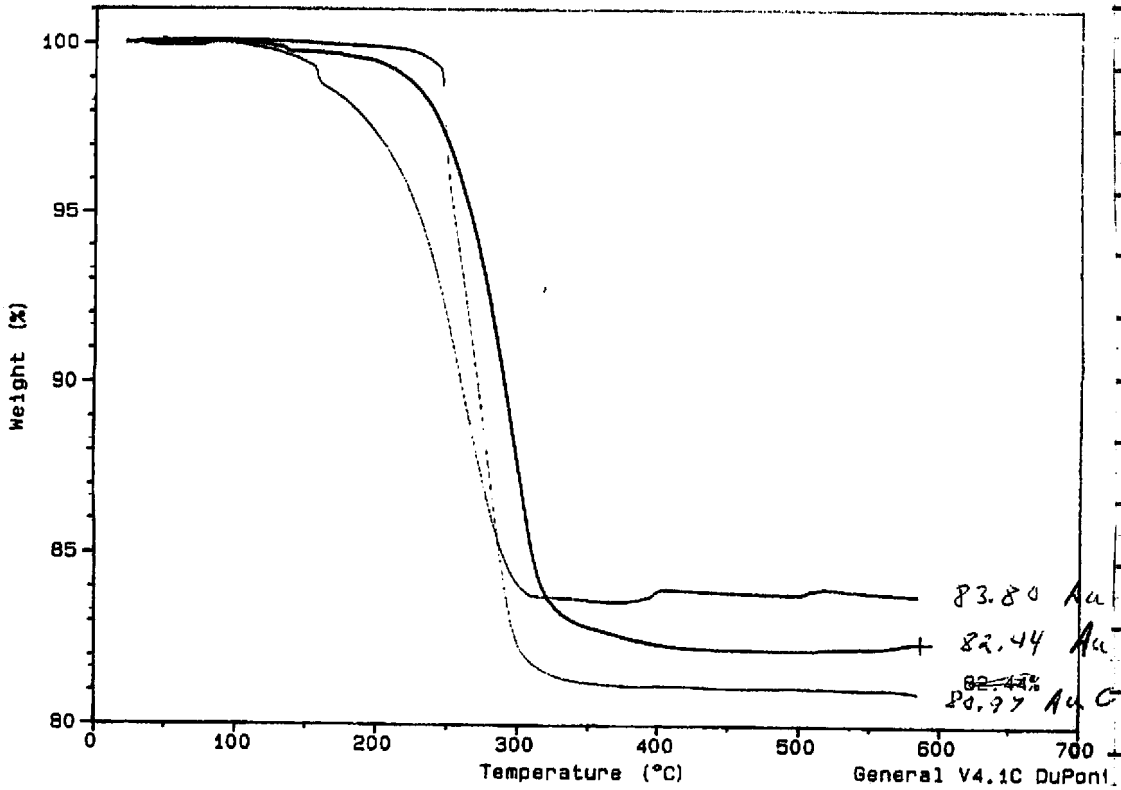
Read and understood (obtain two signatures):

Witness _____ Date _____ Signature _____ Date 6-10-97

Witness _____ Date _____

Sample: AU; C8(3:1) File: A:AUC8.105
Size: 15.0960 mg Operator: AKS
Method: RAMP TO 600 AT 20C/MIN Run Date: 8-Oct-97 22:06
Comment: N-950-80, AU; C8(3:1) VACUUM DRIED, NITROGEN ATM





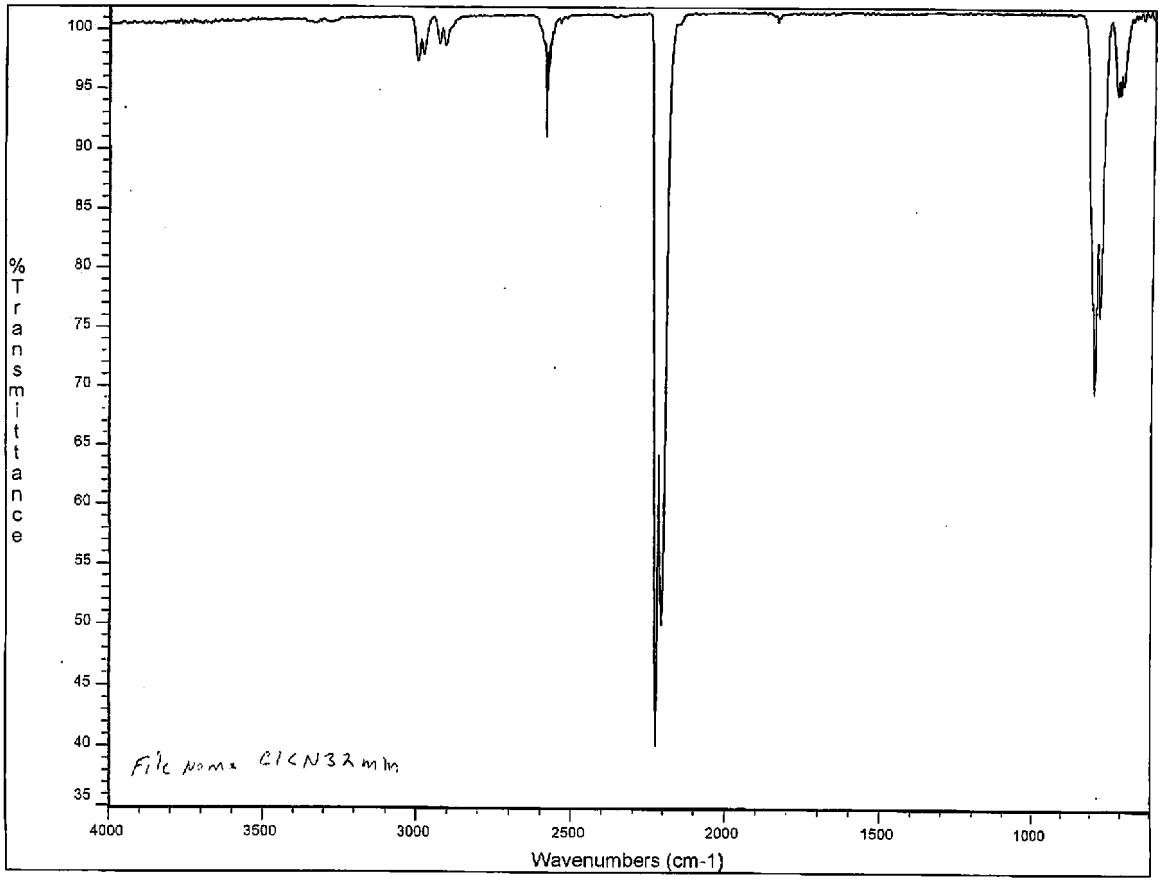
Read and understood (obtain two signatures):

Witness _____ Date _____ Signature _____ Date 5-10-97

Witness _____ Date _____

Cyanogen Chloride

Cyanogen chloride was condensed in a trap at -78°C from a ClCN cylinder (Matheson) transferred to a vacuum line vacuum distilled (-24°C) and ~~[illegible]~~ Transferred to a storage bulb (~700mm) A gas IR spectrum (ClCN 32mm) of the purified vapor was obtained



ead and understood (obtain two signatures):

Witness _____ Date _____ Signature Arthur Snow Date 6-11-97

Witness _____ Date _____

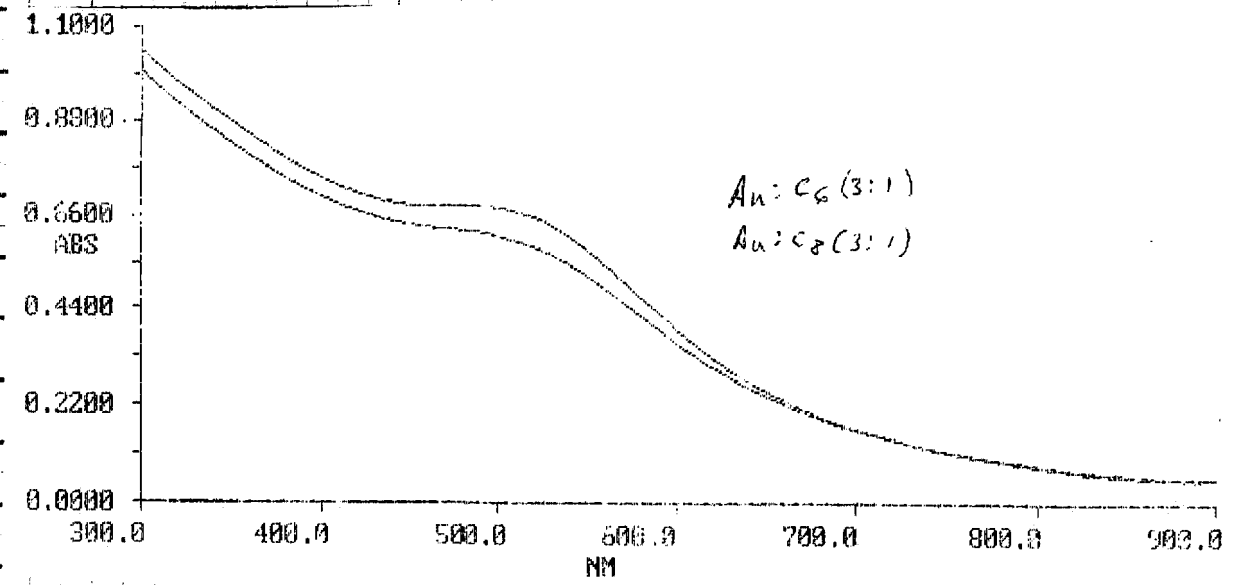
UV-Vis Characterization of AuC_6 (3:1), AuC_8 (3:1), $AuC_2\phi$ (1:1), $AuC_1\phi$ (1:1) and $AuC_1\phi OMe$ (1:1)
(Continuation from NJ 7950-66)

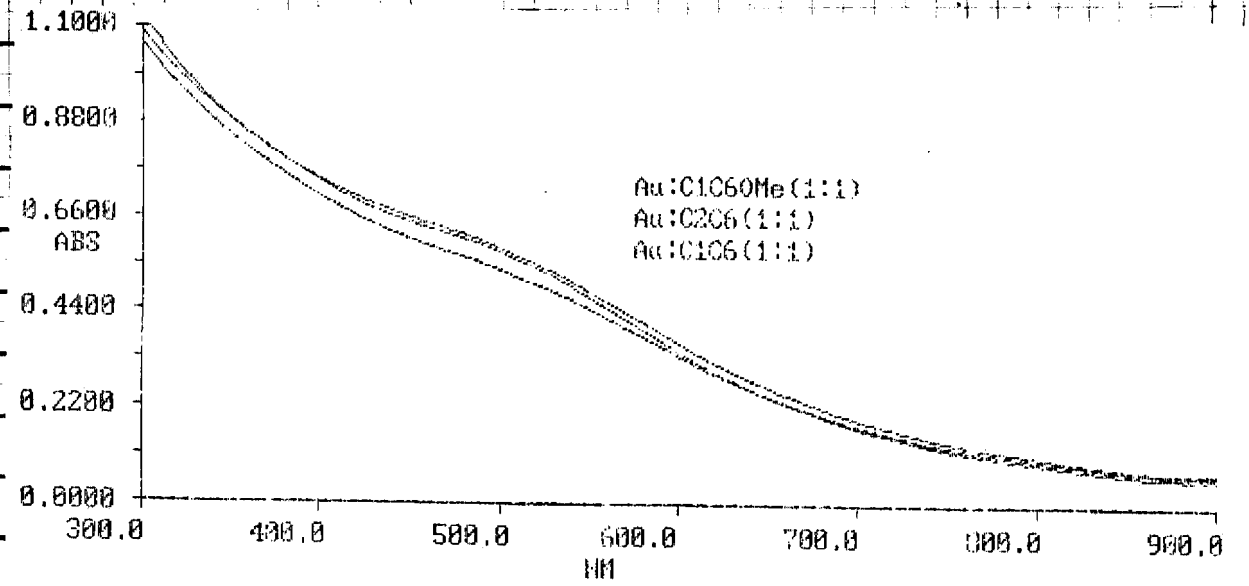
C_6 3:1	1.428 mg / 17.8736 g	5.2420 g CS1 / 10.4045 g	
	0.0799 mg/g	0.0403 mg/g	
	C6 0310 1	C6 0310 2	
	A_{507} = 1.3383	A_{507} = .6765	
	A/bc = 16.75	A/bc = 16.79	a(ε) = 11.3 (2510)
C_8 (3:1)	1.802 mg / 22.5542 g	4.7831 g CS1 / 9.5885 g	
	0.0795 mg/g	0.0399 mg/g	
	C8 0310 1	C8 0310 2	
	A_{507} = 1.2252	A_{507} = 0.6083	
	A/bc = 15.33	A/bc = 15.25	a(ε) = 10.3 (2410)
$C_2\phi$ (1:1)	1.162 mg / 14.5510 g	3.7484 g CS1 / 7.5346 g	
	0.07986 mg/g	0.0397 mg/g	
	C2C6 0111	C2C6 0112	
	A_{507} = 1.1323	A_{507} = 0.5666	
	A/bc = 14.18	A/bc = 14.27	a(ε) = 9.64 (2346)
$C_1\phi$ (1:1)	1.440 mg / 18.0590 g	4.8889 g CS1 / 9.8178 g	
	0.07974 mg/g	0.0397 mg/g	
	C1C6 0111	C1C6 0112	
	A_{507} = 1.0460	A_{507} = 0.5258	
	A/bc = 13.17	A/bc = 13.24	a(ε) = 8.95 (2105)
$C_1\phi OMe$ (1:1)	1.749 mg / 21.9119 g	3.8308 g CS1 / 7.6113 g	
	0.07982 mg/g	0.04017 mg/g	
	C1C6 OM01	C1C6 OM02	
	A_{507} = 1.1358	A_{507} = 0.5749	
	A/bc = 14.23	A/bc = 14.31	a(ε) = 9.67 (2310)

Read and understood (obtain two signatures):

Witness _____ Date _____ Signature Arthur Shu Date 6-11-97

Witness _____ Date _____





Read and understood (obtain two signatures):

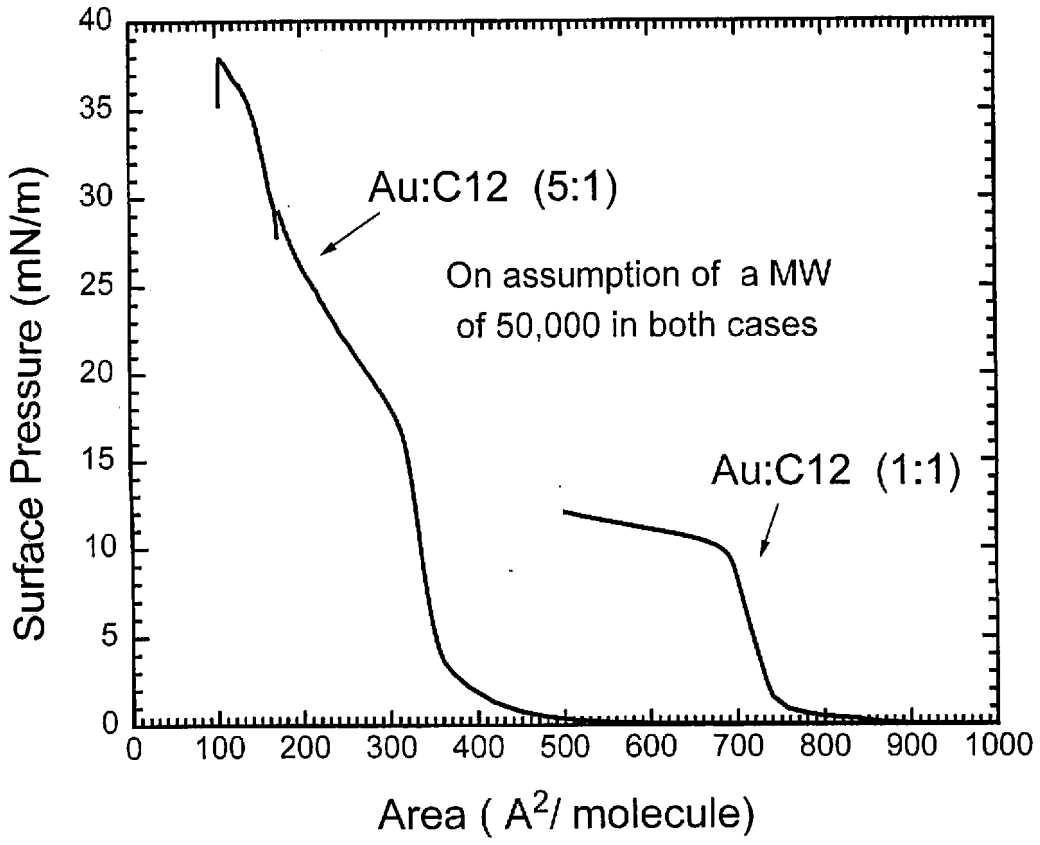
Witness _____ Date _____ Signature Arthur Snow Date 6-1-93

Witness _____ Date _____

Langmuir-Blodgett Isotherm of $Au:C_{12}$ (1:1) and $Au:C_{12}$ (5:1)

Objective: Obtain measure of ligand-shell and void component in packed $Au:C_{12}$ (1:1) and $Au:C_{12}$ (5:1) solids. Also should be able to correlate surface density measurement with bulk density measurement.

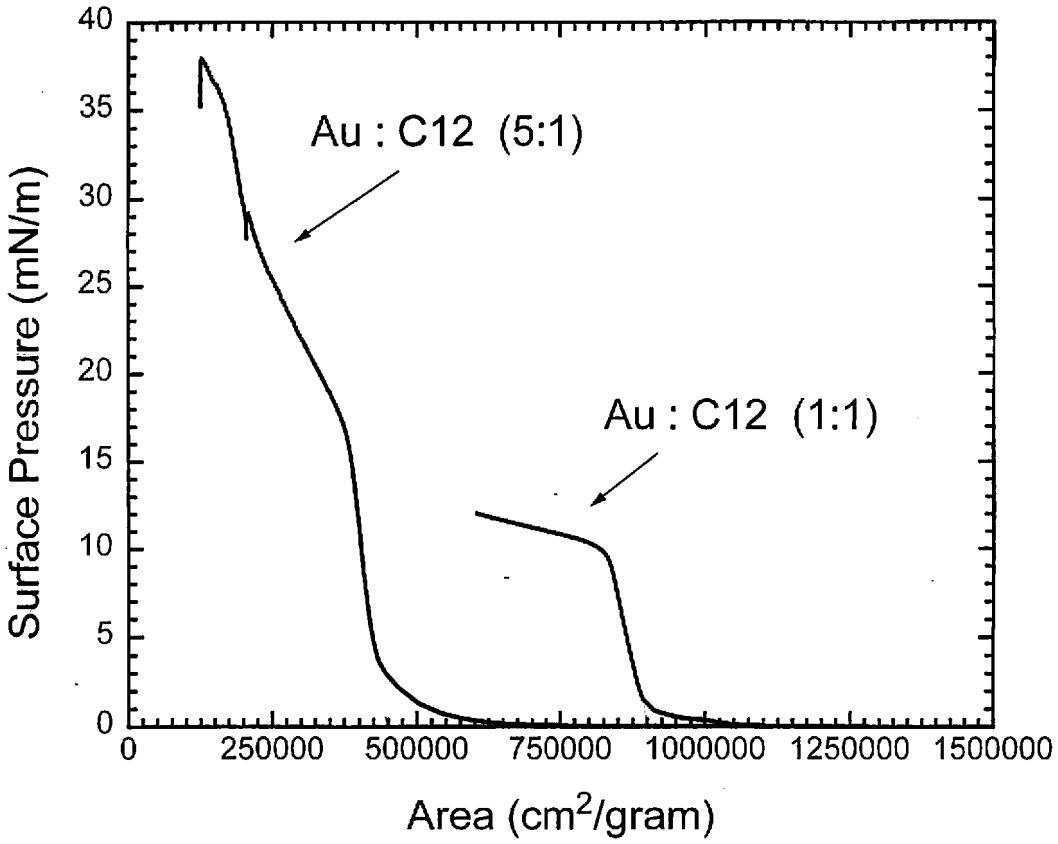
The measurement was conducted by W. R. Barger.



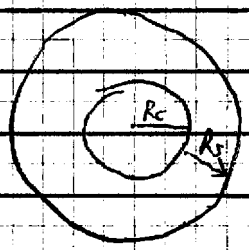
Read and understood (obtain two signatures):

Witness _____ Date _____ Signature Arthur Ulman Date 6-12-97

Witness _____ Date _____



The Following Analysis was derived to utilize the surface densities from the above data



Surface density $\rho' = \frac{M}{A}$

Mass $M = M_c + M_s$

Core Mass $M_c = \frac{4}{3}\pi R_c^3 \rho_c$

Mass Fraction $X_c = \frac{M_c}{M_c + M_s}$ $X_s = \frac{M_s}{M_c + M_s}$ $\Rightarrow M_s = \frac{X_s}{X_c} M_c$

Area $A = A_c + A_s$

$A_c = \pi R_c^2$

$A_s = \pi (R_c + R_s)^2 - \pi R_c^2$ } this expression assumes A_s is given at shallow ν

Read and understood (obtain two signatures):

Witness _____ Date _____ Signature Arthur Snow Date 6-12-89

Witness _____ Date _____

$$\rho' = \frac{M}{A} = \frac{M_c + M_s}{A_c + A_s} = \frac{M_c + \frac{X_s}{X_c} M_c}{\pi R_c^2 + \pi (R_c + R_s)^2 - \pi R_c^2} = \frac{M_c \left(1 + \frac{X_s}{X_c}\right)}{\pi (R_c + R_s)^2}$$

$$\rho' = \frac{\frac{4}{3} \pi R_c^3 \rho_c \left(1 + \frac{1 - X_c}{X_c}\right)}{\pi (R_c + R_s)^2} = \frac{\frac{4}{3} R_c^3 \rho_c \frac{1}{X_c}}{(R_c + R_s)^2}$$

$$(R_c + R_s)^2 = \frac{4}{3} R_c^3 \frac{\rho_c}{\rho'} \frac{1}{X_c}$$

$$\boxed{R_s = \left[\frac{4 R_c^3 \rho_c}{3 \rho' X_c}\right]^{1/2} - R_c}$$

Cluster	X_c	R_c	ρ'	ρ_c
Au_{12} (1:1)	~~.7549~~ ~~.7495~~	~~1.14~~ 0.86 nm	$\frac{15}{900000\ cm^2}$	19.3 g/cm³
Au_{12} (5:1)	.8709	2.97 nm	$\frac{15}{4500000\ cm^2}$	19.3 g/cm³

$$R_{s\,Au_{12}(1:1)} = \left[\frac{4 (~~1.14~~ 0.86\ nm)^3 \cdot 19.3\ g/cm^3}{3 \left(\frac{15}{900000\ cm^2}\right) \frac{.7495}{.7549}} \times \left(\frac{cm}{10^7\ nm}\right)\right]^{1/2} - ~~1.14~~ 0.86\ nm$$

$$= \left[\frac{4.545}{2.047\ nm^2}\right]^{1/2} - ~~1.14~~ 0.86\ nm = ~~0.99~~ 0.93\ nm$$

$$R_{s\,Au_{12}(5:1)} = \left[\frac{4 (2.97\ nm)^3 \cdot 19.3\ g/cm^3}{3 \left(\frac{15}{4500000\ cm^2}\right) .8709} \left(\frac{cm}{10^7\ nm}\right)\right]^{1/2} - 2.97\ nm$$

$$= \left[34.83\ nm^2\right]^{1/2} - 2.97\ nm = 2.93\ nm$$

R_s is not near the same value for the two cluster-complexes. Approximating A_s by πR_s^2 is probably not correct. Modified derivation on next page solves for A_c rather than R_s. Next R_s accommodates void area.

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Witness _____ Date _____

A_s = non Core area in L-B Film

$$\rho' = \frac{M}{A} = \frac{M_c + M_s}{A_c + A_s} = \frac{M_c + \frac{x_s}{x_c} M_c}{A_c + A_s} = \frac{M_c\left(1 + \frac{x_s}{x_c}\right)}{A_c + A_s}$$

$$A_c + A_s = \frac{M_c}{\rho'}\left(1 + \frac{1 - x_c}{x_c}\right) = \frac{\frac{4}{3}\pi R_c^3 \rho_c}{\rho'} \cdot \frac{1}{x_c}$$

$$\boxed{A_s = \frac{4\pi R_c^3 \rho_c}{3\rho' x_c} - \pi R_c^2}$$

$$A_{s_{AuCl_2(1:1)}} = \left[\frac{4\pi (.86\,nm)^3 \; 19.3 \frac{g}{cm^3}}{3 \; \frac{19}{9000000\,cm^2} \cdot .7549} \cdot \frac{cm}{10^7 nm}\right] - \pi (.86\,nm)^2$$

$$= 6.43\,nm^2 - 2.32\,nm^2 = 4.1\,nm^2$$

$$A_{s_{AuCl_2(5:1)}} = \left[\frac{4\pi (2.97\,nm)^3 \; 19.3 \frac{g}{cm^3}}{3 \; \frac{15}{4500000\,cm^2} \cdot .8709} \cdot \frac{cm}{10^7 nm}\right] - \pi (2.97\,nm)^2$$

$$= 109.4\,nm^2 - 27.7\,nm^2 = 81.7\,nm^2$$

	A_s	A_c	$\frac{A_c}{A_c + A_s}$
$AuCl_2(1:1)$	10.20	4.05	.29
$AuCl_2(5:1)$	81.7	27.7	.25

The $\frac{A_c}{A_c + A_s}$ (fraction of area occupied by core) indicates packing is more efficient for smaller cluster

Read and understood (obtain two signatures):

Witness _____ Date _____ Signature Arthur Snow Date 6-12-97

Witness _____ Date _____

Density Measurement of AuC_{12} 1:1 and AuC_{12} 5:1

Objective - obtain density to determine ligand shell and void volume in cluster matrix

Samples of AuC_{12} 1:1 and AuC_{12} 5:1 were prepared by depositing conc. soln's / toluene into 12 mg DSC pans and evaporating and vacuum drying.

AuC_{12} 1:1		AuC_{12} (5:1)	
12.823 mg	Pan	12.642 mg	Pan
26.163 mg	Pan + C_{12} 1:1	46.693 mg	Pan + C_{12} 5:1

A 6 week time lapse occurred between this sample preparation and the measurements below.

A Mettler MT5 (.001 mg sensitivity) balance was used with access to a hangar from below - A platinum wire (very thin) loop in ½ in was placed over the balance hangar rod and a second very thin platinum wire was fashioned with a helical basket at one end and a hook to connect to the loop at the other end as illustrated at right

The balance was zeroed with the loop in place, then the wire basket was connected to the loop, weighed in air, loaded with the sample pan & weighed in air, sample pan removed and basket immersed in water (3X distilled) weighed and sample loaded underwater in the basket and sample weighed under water

Data were taken as follows

Read and understood (obtain two signatures):

Witness Date Signature Arthur Lee Date 6-12-97

Witness Date

Blank	Wire	Wire + pan		Wire	Wire + pan
air	31.91	43.73	±.1	35.95	48.60 ±.1
Water	31.72	39.24	±.1	34.83	43.02 ±.1

$AuCl_2$ (1:1)

	Wire	Wire + pan	
air	35.35	62.27	
Water	35.72	53.23	±.1

$AuCl_2$ (5:1)

	Wire	Wire + pan	
air	35.99	82.26	±.1
Water	35.42	64.50	±.1

Specific Gravity Displacement Ref. ASTM D972-66 p.428

$$sp\ gr = \frac{W_{air,s}}{W_{air,s} - W_{water,s}}$$

$W_{air,s}$ = wt of sample in air = $W_{air,sample} - W_{air,wire}$

$W_{water,s}$ = wt of sample in water = $W_{water,sample} - W_{water,wire}$

Blank #1 $sp\ gr = \frac{(43.73 - 31.91)}{(43.73 - 31.91) - (39.24 - 31.72)} = \frac{11.82}{4.30} = 2.75$

#2 $sp\ gr = \frac{(48.60 - 35.95)}{(48.60 - 35.95) - (43.02 - 34.83)} = \frac{12.65}{4.44} = 2.84$

for Aluminum literature (CRC) sp gr = 2.70

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Witness Date

$AuC_{12}(1:1)$ $Sp\,gl = \frac{(62.27-35.35)}{(62.27-35.35)-(53.23-35.72)} = \frac{26.92}{9.41} = 2.86$

$AuC_{12}(5:1)$ $Sp\,gl = \frac{(82.26-35.99)}{(82.26-35.99)-(64.50-35.42)} = \frac{46.27}{17.19} = 2.69$

These results for the AuC_{12} complexes appear to be low but Blank is accurate

Densities for the AuC_{12} complexes are obtained as follows

Component a = Aluminum pan Component b = AuC_{12} complex

$$\rho = \frac{M_a + M_b}{V_a + V_b} \qquad \rho_a = \frac{M_a}{V_a}, \quad \rho_b = \frac{M_b}{V_b}$$

$$\rho = \frac{M_a + M_b}{\frac{M_a}{\rho_a} + \frac{M_b}{\rho_b}}$$

$$\frac{M_a}{\rho_a} + \frac{M_b}{\rho_b} = \frac{M_a + M_b}{\rho}$$

$$\frac{M_b}{\rho_b} = \frac{M_a + M_b}{\rho} - \frac{M_a}{\rho_a}$$

$$\boxed{\frac{1}{\rho_b} = \left(\frac{M_a}{M_b} + 1\right)\frac{1}{\rho} - \frac{M_a}{M_b}\frac{1}{\rho_a}}$$

$AuC_{12}(1:1)$ $M_a = 12.825$ mg $M_b = 26.163 - 12.825 = 13.338$ mg

$\rho_a = 2.75$ $\rho = 2.86$

$$\frac{1}{\rho_b} = \left(\frac{12.825}{13.338} + 1\right)\frac{1}{2.86} = \frac{12.825}{13.338}\frac{1}{2.75} = 0.336$$

$\rho_b = 2.97$

$AuC_{12}(5:1)$ $M_a = 12.642$ $M_b = 46.693 - 12.642 = 34.051$

$\rho_a = 2.75$ $\rho = 2.69$

$$\frac{1}{\rho_b} = \left(\frac{12.642}{34.051} + 1\right)\frac{1}{2.69} = \frac{12.642}{34.051}\frac{1}{2.75} = 0.374$$

$\rho_b = 2.69$

Read and understood (obtain two signatures):

Witness _____ Date _____ Signature Arthur Snow Date 6-14-97

Witness _____ Date _____

Thickness Calculation of $Au\,C_{12}(1:1)$ and $Au\,C_{12}(5:1)$

$Au\,C_{12}(1:1)$ $\rho' = \frac{1\,g}{90000}$ (page 34)

$\rho = 2.97\ g/cm^3$

$$t = \frac{\rho'}{\rho} = \frac{\frac{1\,g}{90000\,cm^2}}{2.97\ g/cm^3} \times \frac{10^7\,nm}{cm} = 3.7\ nm$$

$Au\,C_{12}(5:1)$ $\rho' = \frac{1\,g}{450000\,cm^2}$ page 34

$\rho = 2.69\ g/cm^3$

$$t = \frac{\rho'}{\rho} = \frac{\frac{1\,g}{450000\,cm^2}}{2.699/cm^3} \times \frac{10^7\,nm}{cm} = 8.3\ nm$$

Comparison with TGA derived result

	t (nm)	$2R_{core}$	$2(R_{core}+R_{shell})$ (page 5)	R_{shell}
$Au\,C_{12}(1:1)$	3.7	2.3	4.0	.88
$Au\,C_{12}(5:1)$	8.3	5.9	8.6	1.35

The agreement between t and $2(R_{core}+R_{shell})$ appears to be very reasonable and perhaps vindicates the apparently low $Au\,C_{12}$ density measurements.

Read and understood (obtain two signatures):

Witness _____ Date _____ Signature Arthur Chen Date 6-14-97

Witness _____ Date _____

Au:C$_1\phi$ (1:1) and Au:C$_1\phi$OMe Coated MS1 302 Devices

Objective: preparation of Au:C$_1\phi$ (1:1) and Au:C$_1\phi$OMe coated devices for toluene, TCE, 1-propanol and N_2O vapor isotherm measurement

Four MS1 302 devices were inspected at 500x, rinsed with $CHCl_3$ and plasma cleaned 12 hr prior to coating. Depositions were done in groups of two

Au C$_1$ CE (1:1) N7957-11) ~~10mg/ml~~ 11.0 mg/1.628 g $CHCl_3$

A 10.0 mg/ml solution was prepared and all brushed onto the pair of cleaned MS1 302 devices mounted and preheated to 120°C. 16 one sec passes. Diagnostic current measurement was made at 50 mV

Au C$_1\phi$ (1:1) #1
146 μA

this compares with a 7.6 μA of Au:C$_2\phi$ (N7957-8)

Au C$_1\phi$ (1:1) #2
577 μA

this appears analously large and it was noted that coated brass of heater developed a gold metallic character. Heating had been continued ~5 min after the deposition - this high number might be the result of a thermal instability

Au C$_1$C$_6$ (1:1) N7957-15) 11.2 mg/1.658 g $CHCl_3$

A 10.0 mg/ml solution was prepared and all brushed onto a pair of cleaned MS1 302 devices preheated to 120°C. The application was 16 one sec passes. A diagnostic current measurement was made at 50 mV

Au C$_1$C$_6$OMe (1:1) #1
19.2 μA

Au:C$_1$C$_6$OMe (1:1) #2
16.2 μA

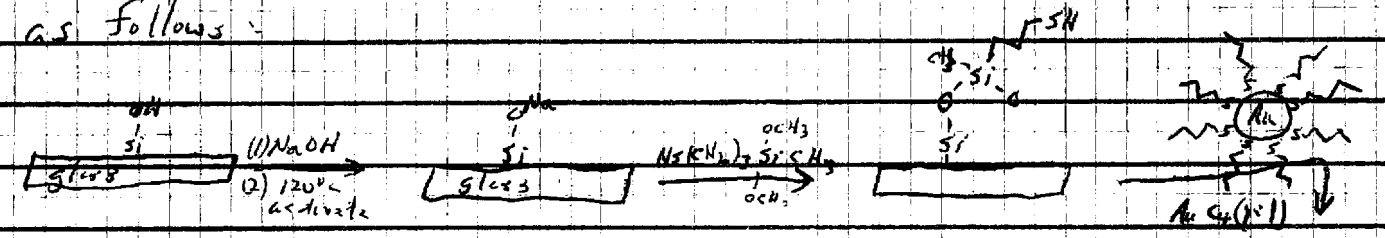
Read and understood (obtain two signatures):

Witness _____ Date _____ Signature Arthur Snow Date 6-19-93

Witness _____ Date _____

Self-Assembly of Au C_4(1:1) / $C_3(SH)_2$ on Glass

Objective: Demonstration that the Au:C_n(X:Y) cluster system can be deposited as uniform films of controlled thickness by a self-assembly technique. Further, these films are stabilized to solvents by intercluster linkage using the difunctional $HS(CH_2)_3SH$. Steps are illustrated as follows:



This concept is also illustrated on N7942-9

The procedure is

(1) A Fisher Plane microscope slide was cut into a 1 x ½ inch rectangular piece.

(2) It was washed in $CHCl_3$ (30 min), 5% NaOH (10 min), 3x distilled water.

(3) Activated by 2 hr at 120°C

(4) Immersed in a 0.061 g $HSCH_2CH_2CH_2Si(OCH_3)_3$ / 0.623 g Hexanes (HPLC grade) for 13 hr

Read and understood (obtain two signatures):

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Witness _____ Date _____

(5) Wash in hexanes 1 min (2 stages of washing)

(6) Immerse in 1.6 mg Au:Cu (1:1) / 2.21 g $CHCl_3$ solution 5 min

(7) Wash 1 min in hexanes sequential dips in two containers

(8) Immerse in 6.8 mg $HS(CH_2)_8SH$ / 2.20 g $CHCl_3$ 5 min

(9) Repeat steps (5) → (8) four times to get 5 layer film.

Each subsequent dip effected effected a darkened intensity of the film (from a faint tinge → an easily perceived dark purple) The film adhered to the glass after washing 20 min with fresh $CHCl_3$. Microscope observation revealed regular features which also appeared on a control blank subjected to cutting treatment. - coloration appeared uniform.

Read and understood (obtain two signatures):

Witness Date Signature Arthur Lee Date 6-29-5

Witness Date